IXTOC OIL SPILL ASSESSMENT
FINAL REPORT

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ABSTRACT

The blowout of the Ixtoc I oil well in the Bay of Campeche resulted in the largest documented spill in history. Approximately half a million metric tons (140 million gallons) of oil were released from the runaway well from June 3, 1979 to March 23, 1980. Of that amount, an estimated 11 thousand metric tons (3 million gallons) impacted south Texas beaches, with an unknown quantity of oil in the waters of the northwest Gulf of Mexico over the biologically productive continental shelf.

As a result of the movement of oil from the Ixtoc I well blowout into the South Texas Outer Continental Shelf (STOCS) environment, a study was undertaken to establish the magnitude and areal extent of perturbation of the benthic community caused by chemical residues of Ixtoc oil. The study focused on the inner shelf region to the 60-metre isobath and examined both the biology and hydrocarbon geochemistry of 12 sites coincident with those of four previously studied (1975-1977) baseline transects. Additionally, 26 sites within the STOCS region sampled during 1979 (mid-spill) for chemical parameters and again in 1980 (post-spill) for chemical and biological parameters, and 39 other sites sampled in 1979 for chemical parameters, were studied. The Burmah Agate oil tanker collided with the freighter Mimosa in November, 1979 5 miles off of Galveston, Texas and spilled part of its cargo of light crude oil into offshore waters. Approximately 21 thousand metric tons (150,000 barrels) of the spilled oil burned in an ensuing fire. As the potentially complicating impact of the Burmah Agate tanker collision was of importance in the STOCS region, a set of six sites in the Galveston region were sampled to gain knowledge of the presence and nature of introduced chemical residues from this event. The study also focused on potential chemical impact on the commercially important penaeid shrimp population from sites within and outside of the primary study region (i.e., the STOCS region).

A blend of analytical chemical techniques was employed successfully to examine a suite of oils/tars taken from the study area beaches and water surface in order to firmly establish the range of compositions of Ixtoc and Burmah Agate oils which might be encountered in the environmental samples (sediments, tissues). High-resolution, fused silica capillary gas chromatography (FSCGC), computer-assisted gas chromatographic mass spectrometry (GC/MS), and stable isotope mass spectrometry (C,H,S) were used together successfully to define the compositional ranges and to identify highly weathered oil residues.

Once these techniques were established, a suite of sediment and shrimp tissue samples were screened for oil by ultraviolet fluorescence spectroscopy (UV/F) to aid in the selection of samples for more detailed analyses. Based on the results from a subset of sediment samples examined by FSCGC, GC/MS, and stable isotope analyses, it was concluded that petroleum residues attributable to the Ixtoc and/or the Burmah Agate spills were not present in the surface sediment anywhere in the study region. Ixtoc oil was, however, detected in suspended sedimentary material at several sites, thus indicating

the presence of oil in the water column system during 1979. Significant quantities of polynuclear aromatic hydrocarbon compounds, products of fossil fuel combustion rather than of direct petroleum origin, were widespread in the sedimentary environment and varied with other geochemical parameters (total organic carbon, grain size). Shrimp tissues examined by FSCGC and GC/MS were shown to be impacted by low levels of chronic petroleum pollutants at many sites, only one sample of which could be linked to Ixtoc residues.

Through biological analyses, precipitous declines in the numbers of individuals and taxa (abundance and diversity) throughout the STOCS study area were found compared with pre-spill measurements. The mid- and post-spill samples differed significantly in numbers of taxa from the fall 1976 and winter 1977 values and differed significantly in numbers of individuals from the fall 1976, winter 1977, and fall 1977 values. Detailed statistical analyses were performed, establishing the grouping of like stations and taxonomic correlations with grain size and total organic carbon parameters.

Since residues of Ixtoc oil were not present in any of the sediment samples, the temporal variations in the benthic macroinfaunal community could not be related definitively to either oil-spill-caused perturbation or to any particular human-induced or environmental factor(s), and may fall within the range of natural variability.

This study established a chemical and biological framework for carrying out spill assessment studies of this nature. It utilized a significant environmental data base for post-"impact" studies for the first time, and identified several sampling methodology deficiencies which, if corrected, may help to fine-tune such assessments in the future.

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SECTION ONE

INTRODUCTION

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SECTION ONE

INTRODUCTION

1.1 General Background

In the last two decades, man's interest in assessing the impacts of his regional and global activities on the "natural state" has led to considerable focus of his energies. Research techniques and tools have been applied, refined, and reapplied to obtain information concerning how ecological systems operate, how a multitude of anthropogenic pollutants are introduced to and transferred between these systems, how (and if) these introductions perturb the system, and how these perturbations affect man. Once they were recognized and popularized, the impacts of industrialization on the coastal marine environment became the focus of many basic and applied research programs.

Pollutant additions to the marine environment fall under one of two general classes: continuous or chronic input, and acute or episodic additions. The chronic addition of certain products of industrial development including petroleum related materials to coastal marine systems has had profound impact on indigenous marine populations and has altered the use of some localized marine environments for significant periods of time (e.g., New York Bight, as a result of ocean dumping). Other chronic inputs, such as those that result in frequent input of tar/oil to the Texas Gulf Coast (Geyer, 1981), have less of an obvious ecological impact, if any. The Brittany coast of France has been acutely affected for several years by the Amoco Cadiz oil tanker spill (CNEXO, 1981) as has the Tierra del Fuego region as a result of the Metula spill (Straughan, 1978). The existence of substantial baseline information allowed major and subtle impacts of oil spills to be detected in the cases of the West Falmouth oil spill (e.g., Burns and Teal, 1979) and the Tsesis oil spill (Linden et al., 1979). An integral part of the impact assessment process is monitoring the return to pre-spill conditions or recovery, as was undertaken for the Zoe Colocotroni (Gilfillan et al., 1981) and Amoco Cadiz (NOAA, 1981) spills.

Offshore exploration and production of petroleum on the Continental shelf was and is a logical extension of land and nearshore production of oil. The goals of the U.S. Department of Interior, Bureau of Land Management's Outer Continental Shelf (OCS) Environmental Study Program are to: (1) obtain environmental data on the impacts of petroleum exploration and production activities on the OCS, and (2) provide relevant information for the decision making (management) process, vis-a-vis offshore minerals management.

The blowout of the Ixtoc I offshore drilling rig in the Bay of Campeche, Mexico on June 3, 1979, resulted in the spillage of 0.5 million metric tons (140 million gallons; 3.5 million bbl) of oil into the Gulf of Mexico (OSIR, 1980) and transport of a significant part of this oil northward into U.S.

coastal waters (Figure 1-1). Surface oil entered U.S. waters on August 6, 1979 (OSIR, 1980) and continued to be seen in significant surface concentrations (i.e. patches of oil, sheen) until the northward-flowing western Gulf of Mexico current reversed during September 1979. The well was finally capped on March 23, 1980. During this period of time approximately 4-11 thousand metric tons (1-3 million gallons) of Ixtoc oil impacted the beaches and seashore intertidal area where oil residues mixed with sand to form tar mats (OSIR, 1980; Gundlach et al., 1981; Tunnel et al., 1981) and perhaps 5 to 10 times as much passed through the Texas OCS region, largely in the form of small patches of emulsified oil (mousse) (Patton et al., 1981), without impacting shore. Approximately 180 metric tons of oil, or less than 5 percent of the total quantity of oil initially beached, was present in the tar mats. The beached oil was largely removed during a tropical storm in September 1979 and either redeposited in the nearshore bar/trough system or taken further offshore. The ultimate fate of the bulk of the oil remains unresolved, although the weathering and physical breakup process described by Patton et al. (1981) and Boehm et al. (1981) followed by distribution of small tarry particles in surface and subsurface waters in the Gulf of Mexico waters seems likely.

Early in November 1979 and still during the Ixtoc I spill, the tanker Burmah Agate, carrying ∿36,000 metric tons (10 million gallons) of oil, collided with the freighter Mimosa approximately 5 miles off of Galveston, Texas (Figure 1-2). The collision caused the Burmah Agate to spill part of its cargo of light crude oil into offshore waters. Kana and Thebeau (1980) have estimated that approximately 21,000 metric tons (150,000 barrels) burned in the ensuing fire. They also estimated that ∿7,000 metric tons (48,000 barrels; 2×10^6 gallons) dispersed offshore during northerly winds. Approximately 10 percent of this oil was recovered offshore, leaving a large portion of the spilled oil to weather by evaporation, photochemical oxidation, etc., or to become mixed in the water column. The fate(s) of the remaining oil include (1) emulsification, dispersion and weathering, (2) mixing with sediment followed by sinking to the offshore benthos, or (3) direct sinking of partly combusted residual oil from the fire. Crude oil exposed to high temperatures, such as those produced during the fire, shows a rapid loss of volatile low-molecular-weight material which may cause an increase in density followed by rapid sinking in seawater (Kolpack et al., 1978). Sinking of large amounts of partly combusted oil and ash was the major fate of oil spilled from and burned during the Sansinena oil spill in Los Angeles Harbor (Kolpack et al., 1978), a similar spill/fire event.

The spilled oil from the Burmah Agate was observed to have an impact on the Texas coast considerable distances from the wreck (∿270 km).

A study of the impact of these spills on the marine environment should focus on an environmental compartment (e.g., offshore benthos) likely to be affected over a long enough time period to facilitate an accurate damage assessment. In the case of the Ixtoc/Burmah Agate spills the circumstances for an accurate damage assessment were favorable because a baseline study of the South Texas Outer Continental Shelf (STOCS) area had been conducted from 1975 to 1977. This baseline information, generated as part of the BLM

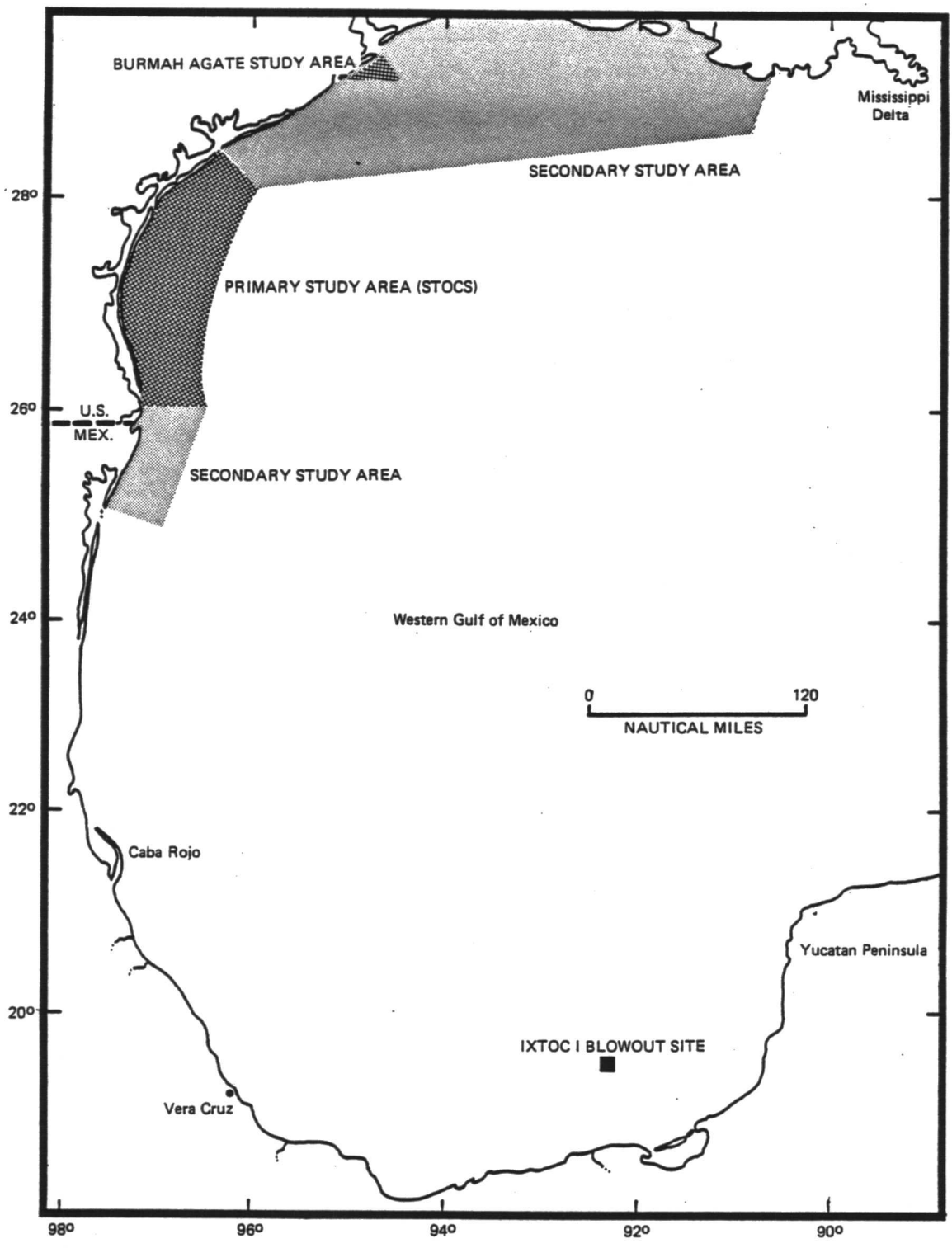


Figure 1—1. Location of Study Areas.

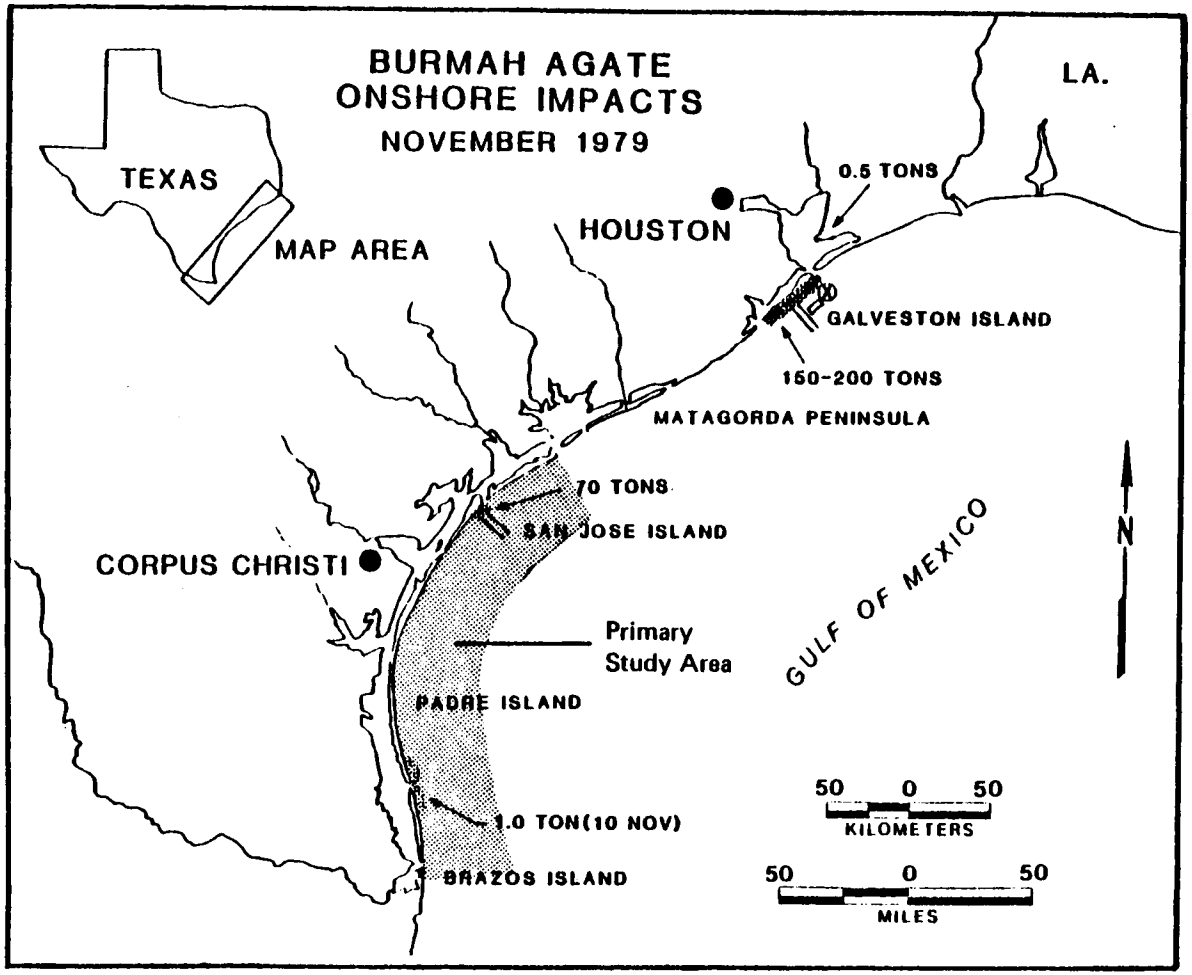


Figure 1–2. Location Map of Burmah Agate Onshore Impacts During November, 1979 (from Kana & Thebeau, 1980).

Environmental Study Program's STOCS program (conducted from 1975-1977) consists of a variety of biological, geological, and chemical oceanographic and biogeochemical data describing the pre-spill state of the OCS region.

In order to direct damage assessment sampling activities and to use this data base (the first such attempt of its kind) successfully, some knowledge of the potential behavior of spilled oil vis-a-vis benthic impact must be incorporated into a study design.

1.2 Transport of Oil to the Benthos

"Weathering" of oil at sea indicates the physical and chemical changes that alter the composition of the petroleum mixture through evaporation, dissolution, photochemical oxidation, and microbial degradation. The physical processes that both mediate these changes and also have subsequent important roles in transport of oil are mixing (dispersion), emulsification, and sorption (NAS, 1975; see Figure 1-3).

It is clear that the extent of long-term biological effects of most oil pollution events studied to date is directly dependent on the extent of oiling of the benthic substrate in and upon which organisms dwell. The existence of oil in the offshore benthos is completely dependent on one or a combination of transport mechanisms which do not come into play when shoreline impacts (marshes, mangrove swamps, intertidal regions) are being studied.

There are several postulated mechanisms by which waterborne petroleum hydrocarbons from an offshore spill event may be transported to the underlying sediment. Three of these mechanisms are presented in Figure 1-4.

There have been few studies directly pertaining to the transport of oil to the offshore continental shelf benthos via the important phenomenon of adsorption of oil on living or detrital particulate matter (or vice versa) followed by sedimentation to the benthos. An evaluation of the possible extent of this process (Figure 1-4) during a spill event is extremely important in order to predict the exposure of important benthic resources to petroleum hydrocarbons released from offshore blowouts. This process is dependent on the availability and concentration of suspended particulates and their surface area (Poirier and Thiel, 1941; Mattson and Grose, 1979; National Academy of Sciences, 1975; Thüer and Stumm, 1977). Another possible route of transport to the benthos is by ingestion of oil by zooplankton followed by fecal pellet transport (Conover, 1971; Johansson et al., 1980). These two processes are those most likely to result in direct water column to benthos transport of petroleum hydrocarbons in continental shelf environments.

Several studies have addressed these mechanisms of transport of oil to the benthos following offshore platform blowouts and tanker spills. Kolpack (1971), and Kolpack et al. (1971) have attributed the large concentrations of oil in sediments following the Santa Barbara blowout to the interaction of petroleum hydrocarbons with sediment-rich river plumes, followed by sorption and sinking. Low but significant concentrations of oil in sediments were

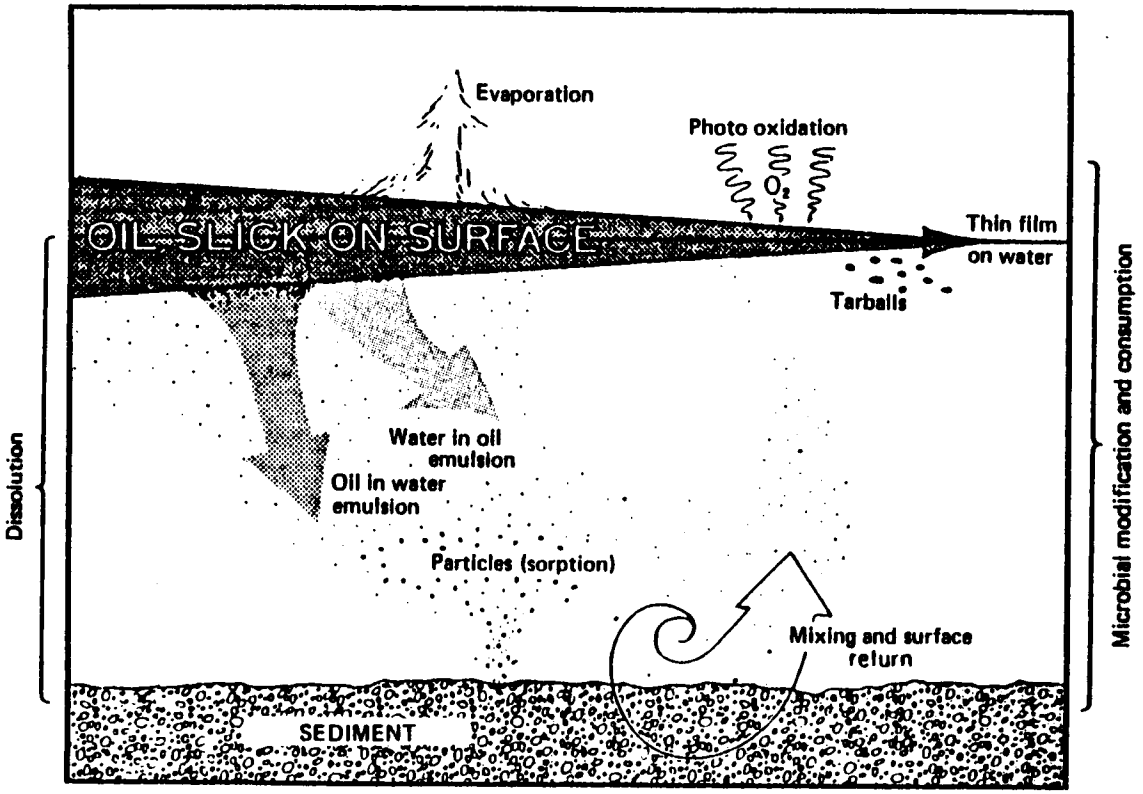


Figure 1–3. Schematic Representation of Weathering Processes and Transport Paths of Spilled Oil at Sea (adapted from, Clark and MacLoed, 1977).

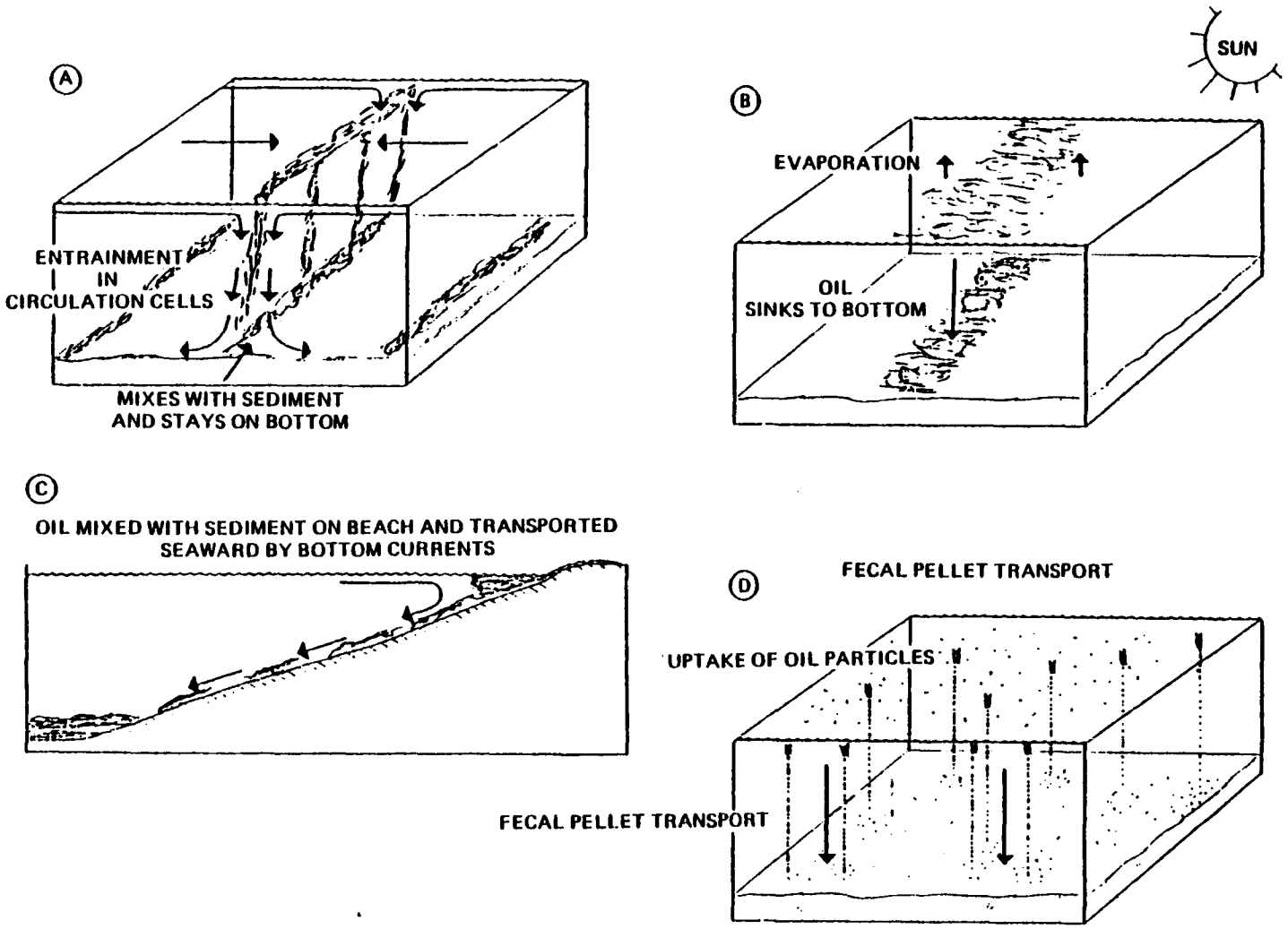
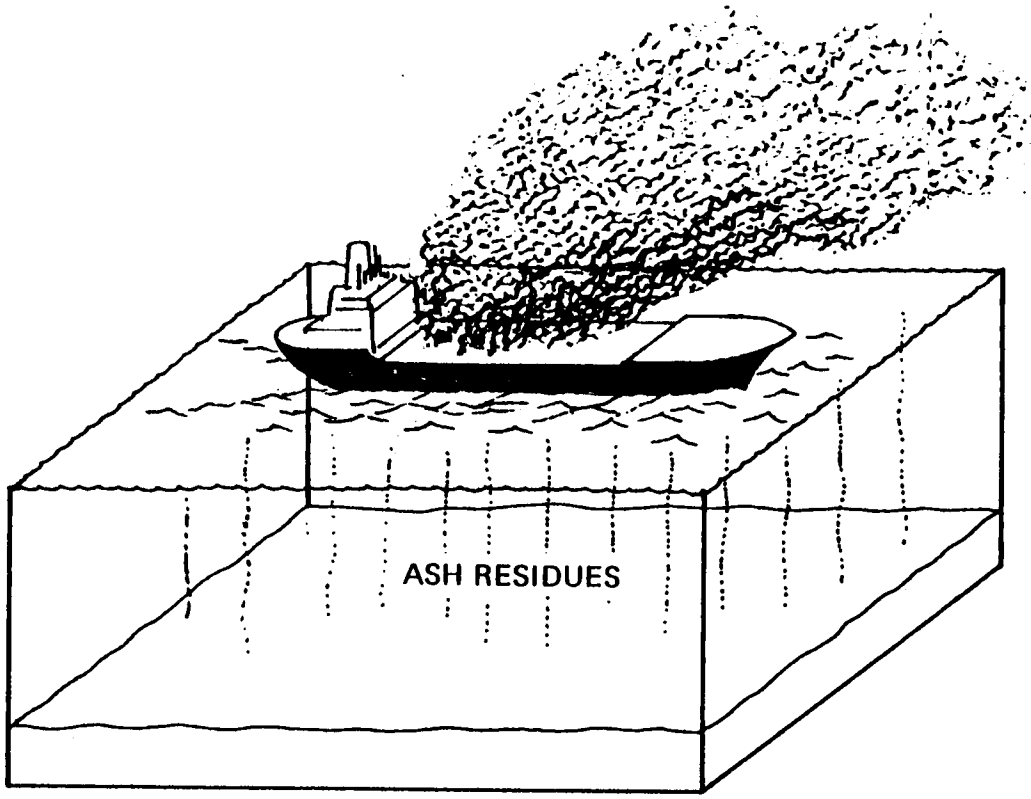


Figure 1–4. Hypothesized Methods by which Oil may be caused to Sink and Remain on the Bottom.



SURFACE OIL FIRE, SINKING OF RESIDUES & ASH

Figure 1–4. (Continued) . Hypothesized Methods by which Oil may be caused to Sink and Remain on the Bottom.

observed following the Ekofisk-Bravo blowout in the North Sea (Johnson et al., 1978) although no specific mechanism was investigated. McAuliffe et al. (1975) have associated the spilled oil in sediments in the vicinity of the Chevron platform blowout at the mouth of the Mississippi River with sorption and sedimentation processes. Boehm et al. (1982) have examined the detailed chemistry of sedimenting oil captured in sediment traps deployed during the Tsesis tanker spill in Sweden. They found that microbial degradation caused rapid alteration of the chemical composition of the spilled cargo, and that the hydrocarbon composition of benthic deposit feeders (Macoma balthica) reflected this composition. Johansson et al. (1980) estimated that 15 to 20 percent of the oil spilled during the Tsesis event was transported to the benthos by sorption and sedimentation and/or by ingestion and zooplankton fecal pellet transport.

The rates of these processes are dependent on the rate and extent of weathering of oil at the sea surface and on mixing energy which disperses oil into the water column in fine droplets, hence increasing the probability of sorption of petroleum hydrocarbons on particulate matter. Sedimentation of oil in offshore environments is thought to be a minor sink for hydrocarbons (Mackay et al., 1979), the extent of which is dependent on suspended sediment loading and biological production (i.e., planktonic concentrations) as well as weathering changes in the oil itself.

The specific gravity of most crude and refined oils spilled at sea does not exceed that of sea water ($\sim$1.025) (Ferraro and Nichols, 1972) and hence direct sinking (Figure 1-4) of petroleum residues at sea is rare. Notable exceptions are spills associated with the Anne Mildred Brovig collision in the North Sea (Mattson and Grose, 1979) and the USNS Potomac (Grose et al., 1979) during which some sinking of oil appears to have occurred probably due to weathering and subsequent fractionation of the oil; and with the Sansinena Bunker C spill (Kolpack et al., 1978) during which the burning of the cargo resulted in the sinking of residuals (analogous to the Burmah Agate situation) (Figure 1-4). Studies of the Ixtoc I emulsified crude oil (mousse) masses off the Texas coast during August 1979 (Patton et al., 1981; Patton and Amos, unpublished data) found that photochemical and evaporative processes presumedly resulted in skinning over and subsequent flaking of mousse patches. Wind-driven dispersion (apparent sinking) drove these neutrally or positively buoyant particles into the water column (Patton et al., 1981).

Petroleum hydrocarbons have become associated with intertidal and subtidal sediments following many spills during which landfall, substrate oiling and offshore transport (Figure 1-4) of affected sediment have occurred. Long-term association of hydrocarbons with sediments has occurred during the West Falmouth (Teal et al., 1978), Chedabucto Bay-Arrow (Cretney et al., 1978; Keizer et al., 1978), and Amoco Cadiz (Beslier et al., 1980; Boehm et al., 1980) oil spills, among others. Similar landfall followed by offshore and hence subtidal transport may have occurred to a great extent during and after the Ixtoc I blowout on both the Mexican and Texas Gulf Coasts. The only documented observations were recorded off the southern Texas coast, where the formation of "tar mats" resulted (Gundlach et al., 1981).

In a study designed to quantify the extent of water-column-to-benthos transport of Ixtoc I oil through sampling and analyses of sedimentary particles (sediment traps) and surface sediment from the wellhead to the Texas coast, Boehm and Fiest (1980b) found that only minor amounts of oil reached the offshore benthos in the vicinity of the wellhead by mechanisms A and B (Figure 1-4). The extent of offshore transport of oil by mechanisms C and D remains unexplored.

Given the Ixtoc spill's history, the beaching and apparent offshore transport of petroleum, and the existence of significant amounts of suspended matter in the water column of the STOCS region, one would expect that detectable sedimentary petroleum residues would be revealed.

In this light, the BLM contracted ERCO and its subcontractors, LGL Ecological Research Associates, Global Geochemistry Corporation, and Geomet Technologies, to undertake a detailed assessment of the impact of the Ixtoc spill and the Burmah Agate "complications" on the offshore benthos of the STOCS region.

1.3 Study Objectives

The primary objectives of the Ixtoc assessment study are to examine and quantify the chemical impact of the Ixtoc and Burmah Agate spills on the offshore benthic environment and to determine if such impacts resulted in sustained perturbation of the benthic biological community. Thus while the study relies heavily on information contained in samples from the Texas beaches and from the wellhead region, the assessment study focuses on the offshore Texas OCS (Figure 1-5) from an area seaward of the offshore bars ($\sim$3 meters depth) to the 60-meter depth contour some 30-40 miles offshore. A second objective was to determine to what extent and for what duration an important commercial fisheries resource, the shrimp fishery, had been chemically affected as a result of these specific spills.

The integrated damage assessment strategy for this project involved the following elements:

1. Determination of what habitats have been affected.

2. Determination of the nature and extent of the chemical impact.

3. Determination of whether biological and ecological perturbations resulted from this impact as compared to both the pre-spill environment (baseline information) and the unaffected environment (reference stations).

4. Determination of a causal relationship between any observed biological changes and the chemical impact.

5. Determination of damage to a commercially important resource (shrimp fishery) due to the chemical impact.

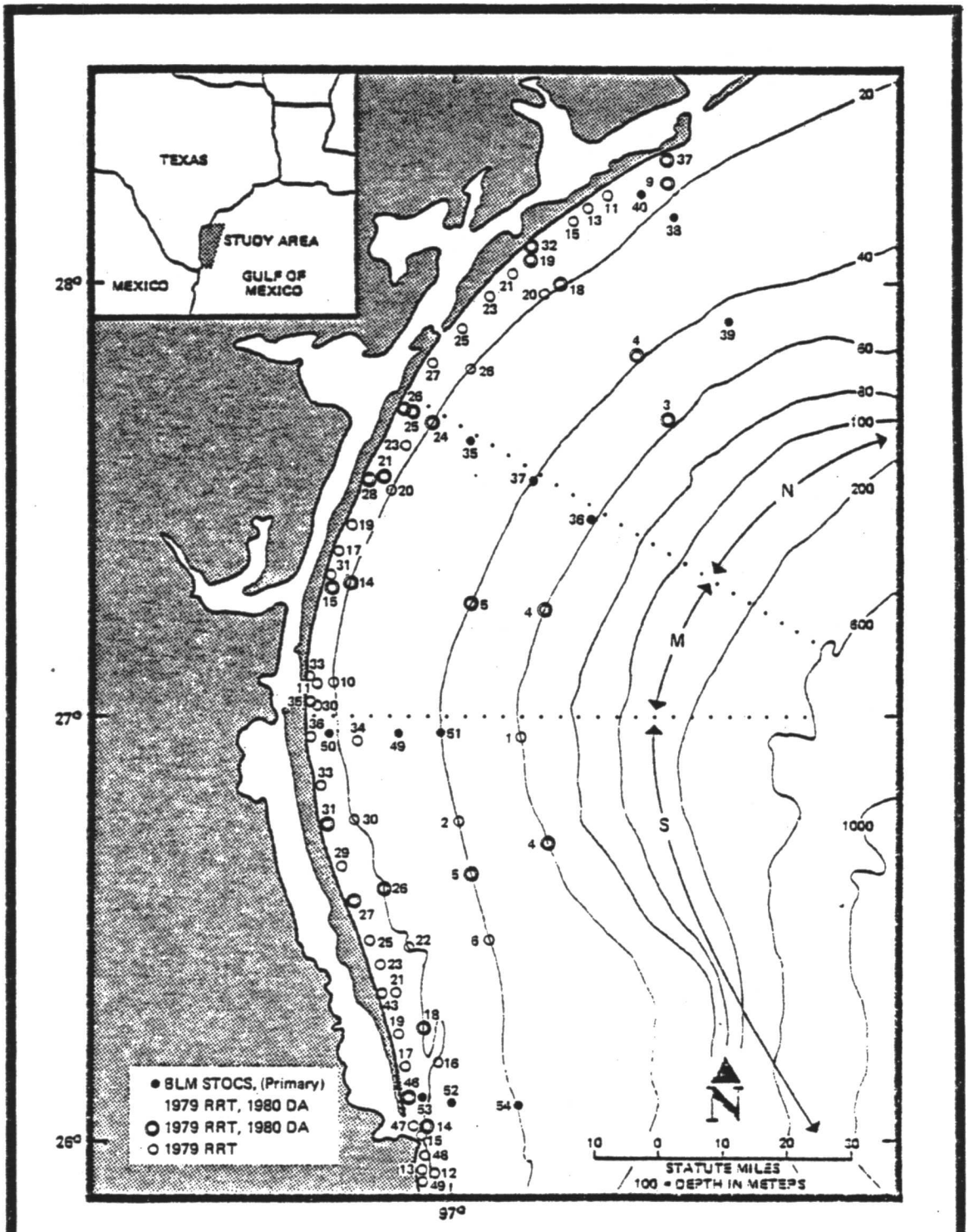


Figure 1–5. Master Locator Map (STOCS Region).

6. Determination of the pre-spill value of the ecological and/or commercial resource and the extent to which its use and/or value has been diminished.

Elements 1 and 2 are chemical questions whose answers define the exposure of an ecological system to contaminants from a particular spill. A detailed chemical-source fingerprinting has to be combined with a knowledge of possible weathering sequences to identify locations within habitats specifically affected by a spill event (Sections 2 and 3). Element 3 involves an analysis of the detailed biota, its abundance and diversity, and a comparison of pre-spill measurements with a knowledge of the range of natural variability (Section 4). Element 3 then draws on the results of 1 and 2 to address element 4. Impacts on commercial species, which affect marketability and human health, are separately defined through chemical analyses of tissues specifically directed to quantification of toxic aromatic hydrocarbons. The assignment of pre-spill "value" is beyond the scope of this project, but the overall goal of assigning an "extent of damage" in a quantifiable form from the biological data is central to the damage assessment strategy.

1.4 Project Strategy

As no comprehensive offshore damage assessment of this nature has previously been undertaken, we feel that the best way to accomplish the program's objectives is to address specifically the impacts of the spills under consideration and to establish and test our methodologies under the broader context of "damage assessment methodology development." Therefore in many cases, new techniques and their applications have been used singly or in combination to address the program's objectives. These will be explored in more detail in the technical chapters.

The basic elements of the project strategy were to:

1. Obtain a set of biological, chemical, and supportive data from samples obtained during Regional Response Team activities, August-December 1979 (i.e., mid-spill) (see NOAA, 1982).

2. Obtain a set of biological, chemical, and supportive data from samples obtained during the December 1980 Tonya and Joe cruise (i.e., post-spill).

3. Compare mid- and post-spill biological and chemical "conditions" with each other and with pre-spill "conditions" (BLM-STOCS program).

4. Examine possible cause-and-effect relationships by synthesizing biological and chemical measurements.

5. Define magnitude and areal extent of Ixtoc spill-related damage.

In order to achieve the program's basic objectives as previously outlined, two sets of environmental samples, one from the mid-spill time period (mid to late 1979) and one from the post-spill time period (late 1980), were obtained. From these samples biological and chemical information was extracted by a variety of methods and compared to the substantial pre-spill (1975-1977) data on similar samples. This latter set, from the STOCS/BLM-sponsored benchmark program, provided a base with which to compare the pre- and post-spill biological and chemical data. The value of the spill assessment program depends upon its ability to detect environmental changes and to assign them to proper causes. The STOCS program included a variety of environmental measurements made over a 3-year period (1975-1977) and therefore represents a potentially valuable source of information, especially with regard to temporal variations in biological and chemical parameters.

All program elements operated independently, as indicated in Figure 1-6, until causal relationships were explored during the data synthesis effort.

1.5 Sample Collections

A variety of samples were collected for the chemical analysis program. Three basic sets of samples were collected:

1. Samples designed to aid in establishing the possible range of "chemical signatures" of weathered Ixtoc and Burmah Agate oils.
    a. Floating oil/tars.
    b. Beached oil/tars.
2. Samples designed to establish the presence of oil in the offshore benthic environment.
    a. Surface sediments.
    b. Sorbent pad samples (water-column-borne oil/resuspended sediment).
3. Samples designed to establish spill impact on epifaunal populations.
    a. Penaeid shrimp.

The biology program relied on collections of benthic infaunal organisms from sediment grab samples.

The geochemical support program included determinations of sediment texture or grain size distributions for all benthic biological samples and sedimentary total organic carbon (TOC) on benthic biological and chemical samples.

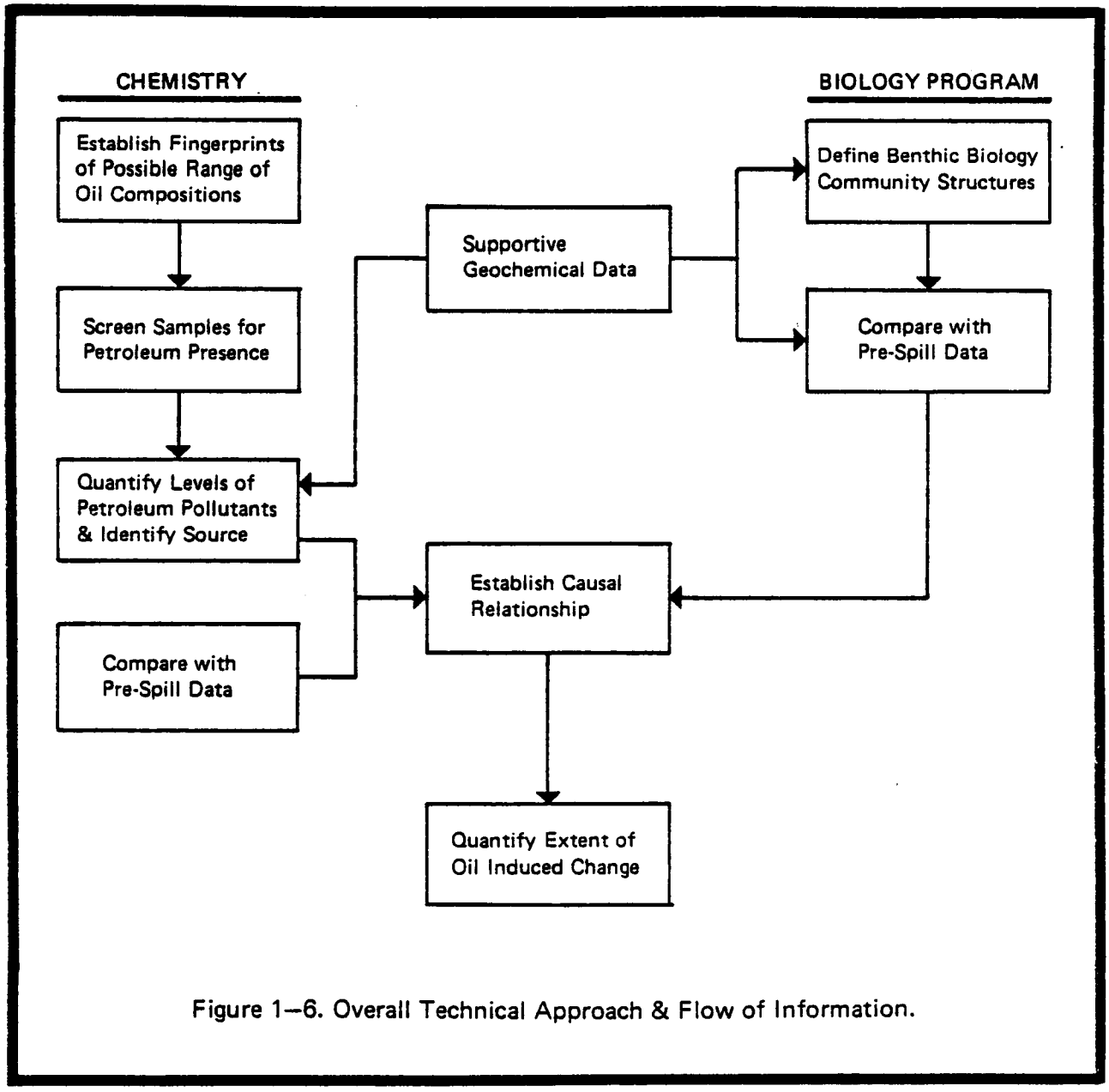


Figure 1–6. Overall Technical Approach & Flow of Information.

Details of the nature of each collection and sampling technique employed are found in Sections 2 and 4, in Appendix 9-1 and in the "Summary Cruise Report," January 15, 1981 (BLM, New Orleans OCS office).

The acquisition of samples centered on four cruises conducted in 1979 (mid-spill) and one undertaken as part of this project during late 1980 (see Table 1-1). The biology program and geochemical support program utilized samples from the Longhorn IV and Tonya and Joe cruises, while the chemical program relied not only on samples taken from these cruises, but also on some obtained during the Western Gulf cruise and on several other collection programs shown in Table 1-2.

1.6 Project Organization

Four organizations participated in the study. Their roles are indicated in Figures 1-7 and 1-8.

TABLE 1-1

SUMMARY OF CRUISES

	VESSEL & SPONSOR	DATES	OBJECTIVES
1.	Valiant (USCG)	July 16-21 (1979)	Collect surface current data on Western Gulf Continental Shelf; log oil locations; collect oil samples
2.	Point Baker (USCG)	July 27-29 (1979)	Sample oil in Mexican waters
3.	Cruise FSU-I (NSF)	July 26-31 (1979)	Emplace deep-ocean current water arrays; test on-board research equipment; log oil locations; collect oil samples
4.	Longhorn I (USCG)	Aug 4-8 (1979)	Search for oil in water column off Texas coast; collect oil, water, and biological samples; take oceanographic measurements
5.	Longhorn II (USCG)	Aug 15-22 (1979)	Survey oil concentrations along Texas/Mexico coastline; observe physical condition of oil
*6.	OSV Antelope (EPA)	Aug 25-Sep 8 (1979)	Determine surface and sub-surface oil distribution and physical form; determine composition of oil and estimate toxicity; test sediments and biological samples for microbiological analysis
*7.	Researcher/Pierce (NOAA)	Sept 11-27 (1979)	Determine effects of oil weathering on marine environment; estimate microbial effects on weathering; study effects of oil on bacteria and plankton
*8.	Western Gulf (NOAA/NMFS)		Seafood sampling

TABLE 1-1 (CONT.)

	VESSEL & SPONSOR	DATES	OBJECTIVES
9.	Cruise FSU-II (NSF)	Oct 31-Nov 6 (1979)	Recover current meter arrays deployed on FSU-I; study the thermohaline structure of the water column; log oil locations; collect samples for geochemical analysis
*10	Longhorn IV (USCG)	Nov 16-Dec 13 (1979)	Survey bottom oil distribution in the offshore, nearshore, and pass areas of South Texas
*11	Tonya & Joe (BLM)	Dec 2-Dec 13 (1980)	Damage assessment offshore benthos and shrimp sampling

*Samples obtained and used for this project.

TABLE 1-2

SUMMARY OF ADDITIONAL SAMPLE COLLECTION EFFORTS

COLLECTION NAME	COLLECTOR	TYPE OF SAMPLES	LOCATIONS	DATES
RPI	various	beached oil and beach sediment	South Texas barrier beaches	July-Sept 1979
Hooper	C. Hooper	floating tar balls	South of Corpus Christi to Mexican border	12-14 Aug 1979
URS	Sturtevant	beached oil/tar	South Texas beaches	Nov/Dec 1979
NOAA Beach Survey	Ernst, Hannah	beached oil/tar	South Texas beaches	1979/1980
Burmah Agate	Coast Guard	oil in water beached oil	Galveston area	Nov 1979
RPI-II (Burmah Agate)	various	beached oil	San Jose Island area	Nov 1979
Dockside Sampling	FDA	shrimp	Shrimp landings (S. Texas)	Summer/ Fall 1979

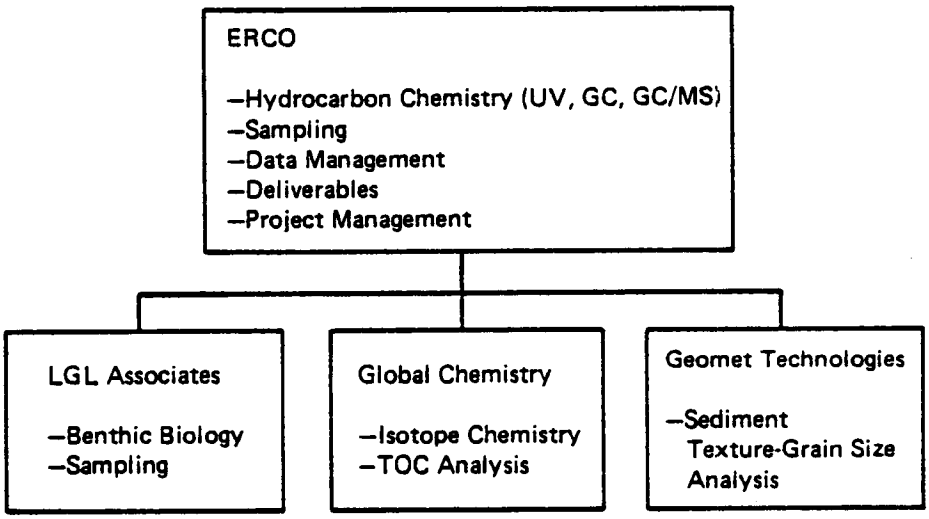


Figure 1–7. Organizational Overview Showing Major Responsibilities of Each Participating Group.

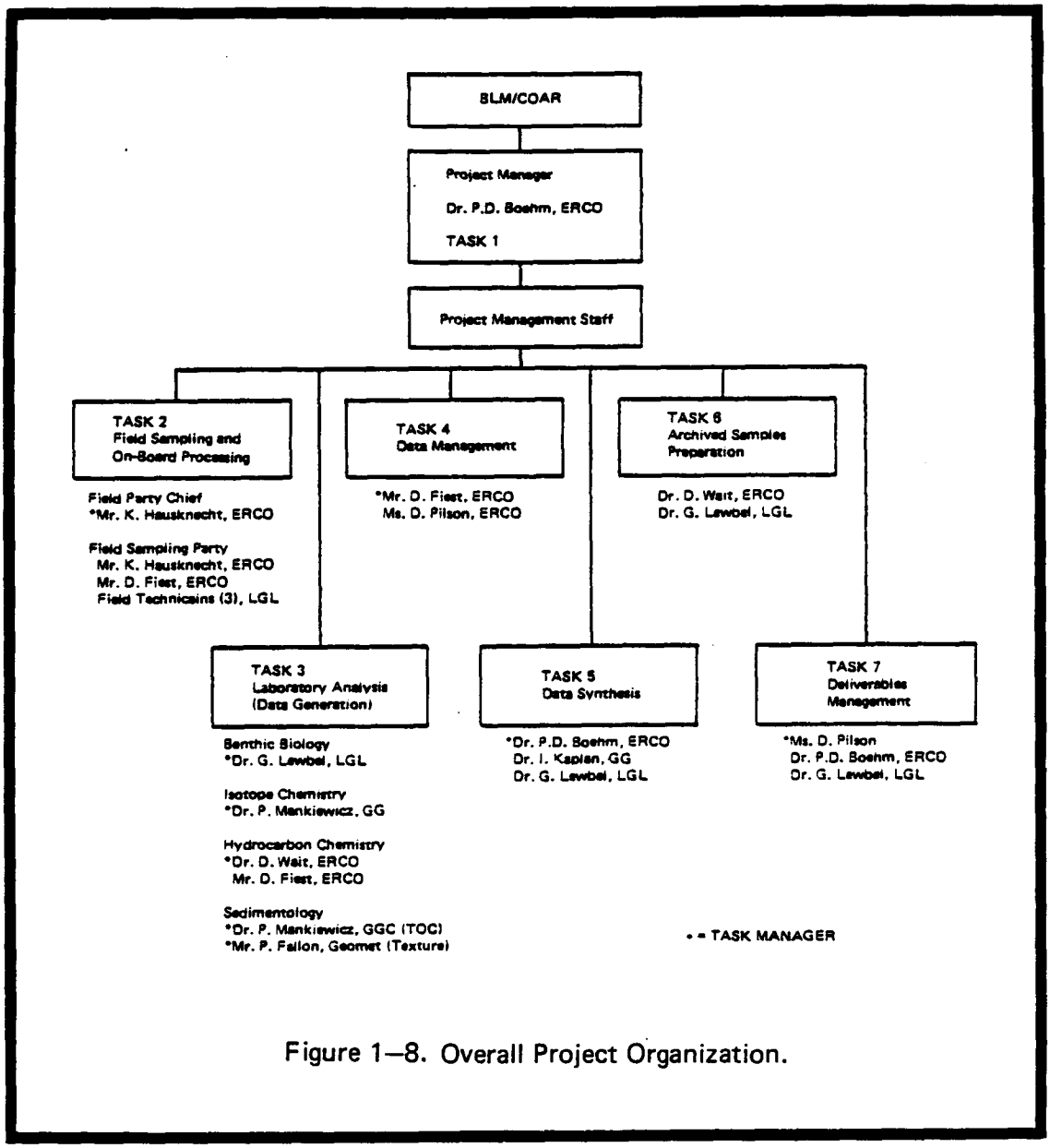


Figure 1—8. Overall Project Organization.

SECTION TWO

CHEMICAL ASSESSMENT - HYDROCARBON ANALYSES

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SECTION TWO

CHEMICAL ASSESSMENT (HYDROCARBONS)

2.1 Introduction

The Ixtoc I blowout occurred on June 3, 1979 but it was not until approximately two months later that oil entered the primary study area shown in Figure 1-1. Transport time of the oil ranged from perhaps a week or so during maximum northward current flow to several months during the initial impact. While the oil was being transported northward to the Texas coast the chemical composition of the oil was altered due to the collective set of chemical, biochemical, and physical processes known as "weathering."

An integral part of the establishment of cause-and-effect relationships between pollutant burdens and biological impact, which is the heart of damage assessment studies, is the establishment of the nature (chemical composition) of the source oil. In this case the source of oil to the Texas OCS benthos is a substantially altered (weathered) Ixtoc I oil. Once the composition or range of compositions of these oils is established, the pollutant burden of the benthic substrate (sediment) and tissues of impacted organisms can be examined.

In the chemical segment of the damage assessment studies there are seven consecutive questions that must be addressed: (1) What is the range of chemical compositions of the pollution (oil) that one can expect to affect the ecosystem being studied? (2) What are the best chemical parameters to use to relate presence of oil in samples to a source? (3) Is there evidence of petroleum hydrocarbons (PHC) in environmental samples? (4) What are the source(s) of these compounds? (5) What are the levels of PHC in the samples? (6) What is the areal extent of contamination? and (7) Does the extent of chemical impact change with time?

To address these questions, we must consider the possible transport and weathering processes that may act on week-to-month-old oil from the Ixtoc I spill or week-old weathered or burned oil from the Burmah Agate collision and spill. These weathering processes, which serve to alter an oil's chemical fingerprint and alter the levels of potential toxicants, are schematically presented in Figure 1-3. The various processes shown in this figure have received attention in recent years, both in laboratory-sponsored programs such as the Marine Ecosystems Research Laboratory (MERL) experiments (e.g., Gearing et al., 1980), NOAA's Multivariate Experimental Analysis of Petroleum Weathering, and in field programs undertaken during spills of opportunity such as the Potomac (Grose et al., 1979), Tsesis (NOAA, 1980a), Amoco Cadiz (CNEXO, 1981), and Ixtoc I (NOAA, 1980b). Of concern in the present study is an understanding of (1) how oil changes chemically in transit from the source to the study area, (2) how oil may be transported to the benthos, (3) how oil may change chemically in the process, and (4) how oil may be taken up and chemically altered by marine organisms once it gets in the benthic substrate.

In the case of Ixtoc I oil spill, a significant amount of information has been previously generated (Boehm et al., 1981a; Boehm and Fiest 1980a,b; Patton et al., 1981) regarding compositional changes observed in the processes of transport via the water column, at the sea surface, and in sedimentation to the benthos.

Incorporation of petroleum into the sediment usually results in accelerated weathering of oil in oxygenated substrate mainly through microbial degradation (Teal et al., 1978; Cretney et al., 1978; Keizer et al., 1978; Beslier et al., 1980; Atlas et al., 1981; Boehm and Fiest, 1980b). Boehm et al. (1980) have conducted a comprehensive study of how Amoco Cadiz oil changed markedly in its composition with time after deposition in intertidal sediments (Figure 2-1). Oil buried beneath the oxygenated zone is subject to little or very slow anaerobic degradation (Ward and Boehm, unpublished data). Even in nutrient-poor waters such as those encountered during the Ixtoc I (NOAA, 1980b) Researcher cruise, where extremely slow rates of biodegradation in the water column were observed (Pfaender et al., 1980; Atlas et al., 1980; Boehm and Fiest, 1980b), incorporation of oil into the offshore sediment accelerated microbial degradation presumably due to the oil's closer proximity to recycled nutrients (Boehm and Fiest, 1980c; Atlas et al., 1981). Therefore, oil transported to the benthos in small-to-moderate quantities can be expected to lose much of its obvious fingerprint (i.e., that based on n-alkane distributions) if the hydrocarbons are available to microorganisms. Pelagic tar balls are notorious exceptions to this rule, maintaining characteristic paraffinic patterns for considerable periods of time (Butler et al., 1973).

It is well known that highly weathered petroleum can begin to lose its easily identifiable characteristics. The paraffinic fraction can be altered by oxidation and isomerization (Figure 2-1), which is followed by alteration of the aromatic fraction. Highly weathered oil requires detailed study by sophisticated analytical procedures such as gas chromatographic mass spectrometry to gain successful molecular characterization.

By contrast, examining weathered oil at the atomic level through the isotopic composition of carbon, sulfur, and hydrogen has been suggested as a technique that succeeds due to the invariant atomic (isotope) signature of petroleum residues (see Section 3). This multiparameter approach was first used by Sweeney and Kaplan (1978) for the characterization of California beach tars using sulfur, carbon, and nitrogen isotopes. The approach was extended to include hydrogen-deuterium isotopes in a study concluded by Sweeney et al. (1980) on mousse and tar from the Ixtoc I oil spill. These studies demonstrated that stable isotope measurements could successfully differentiate tars from various sources.

There has been considerable research in recent years on mechanisms of uptake and depuration of petroleum hydrocarbons by marine organisms (see reviews of Anderson, 1975, 1978). Several important factors bear on successful fingerprinting of petroleum sources from tissue-derived chemical analysis. It is becoming more apparent that many organisms possess their own enzyme systems to metabolize petroleum components (e.g., Payne and Penrose, 1975),

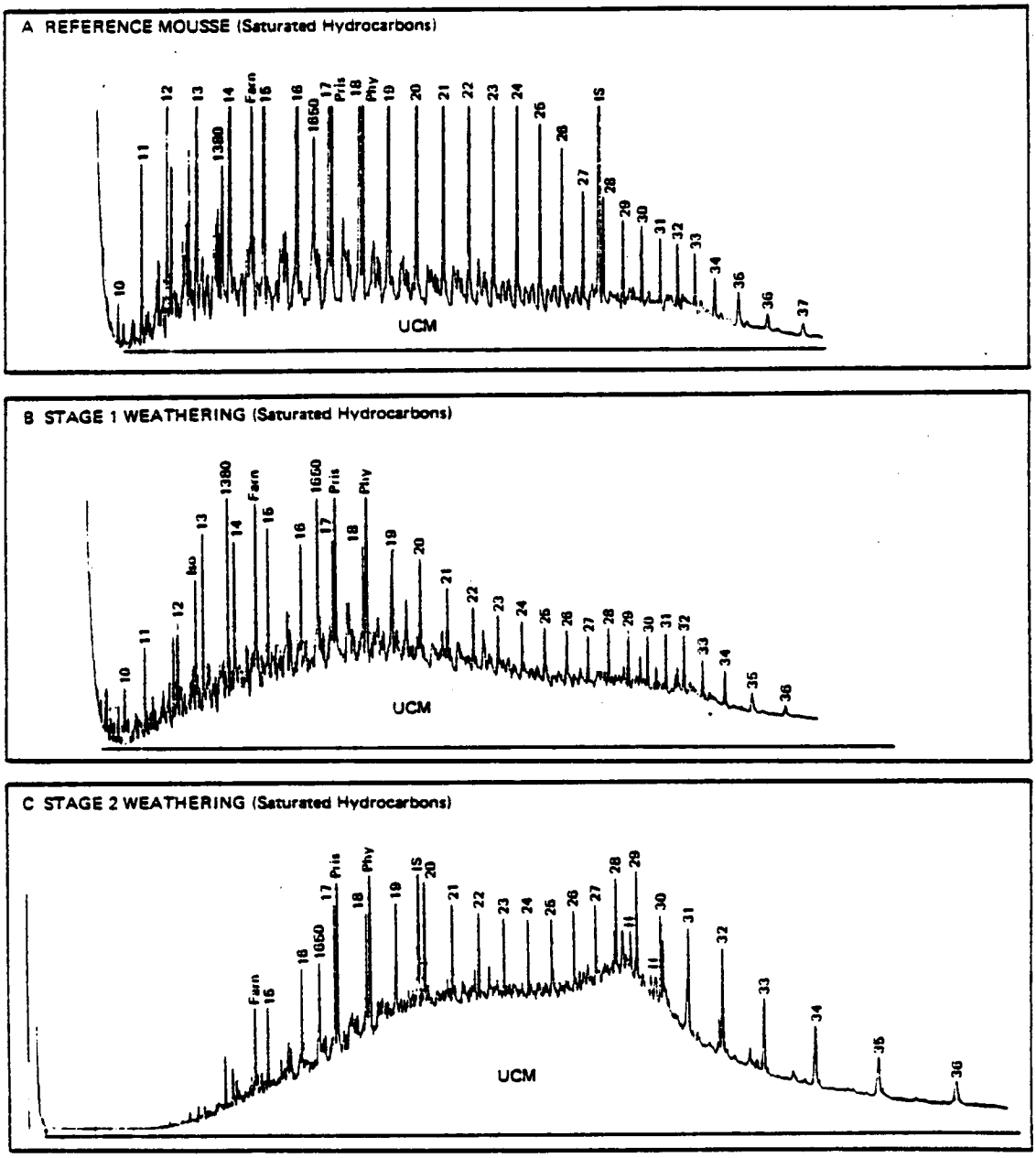


Figure 2–1. Gas Chromatograms Illustrating Weathering Patterns of Saturated Hydrocarbons in Amoco Cadiz Oil (from Boehm et al., 1981b).

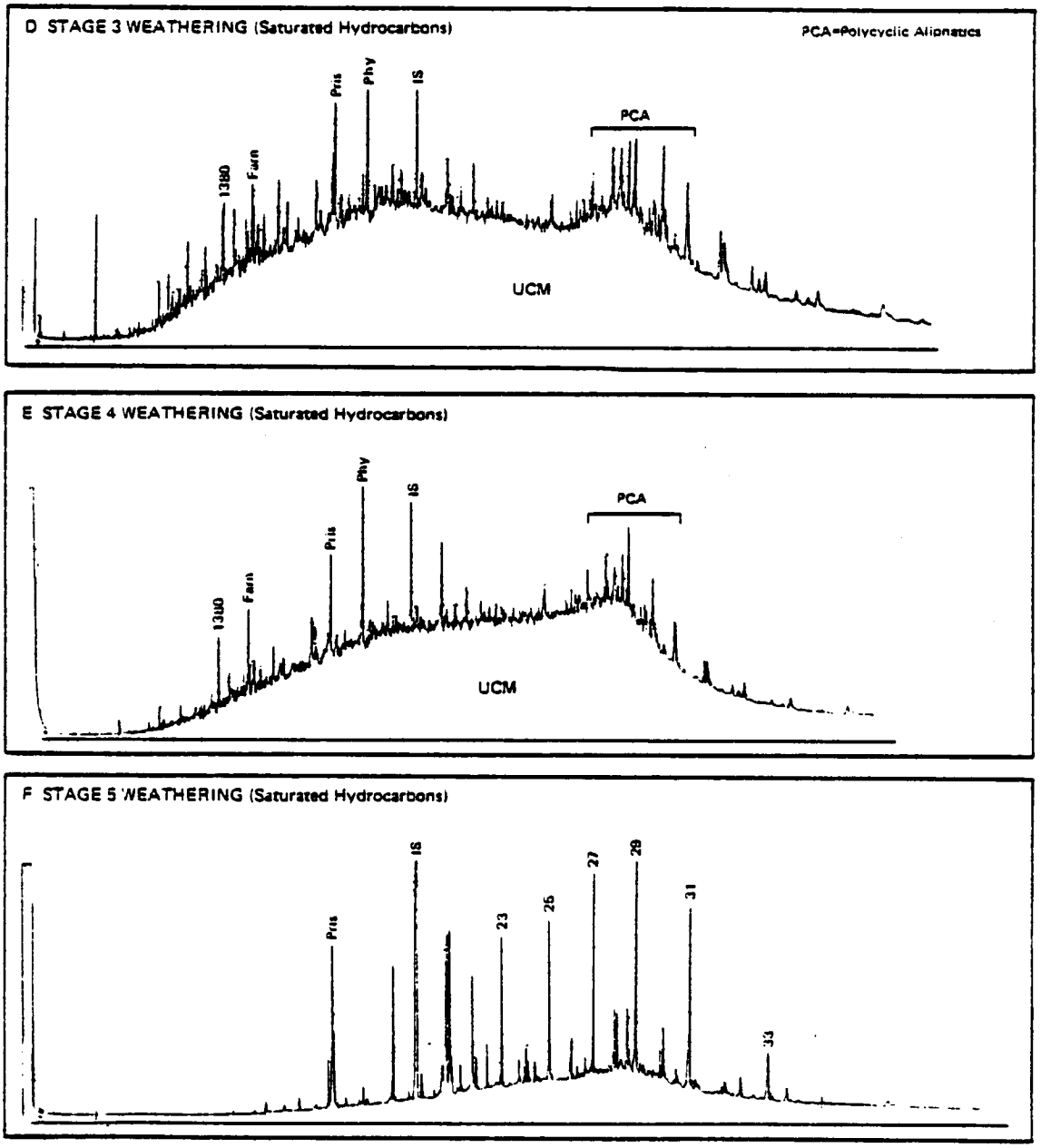


Figure 2–1. (Continued).

although there is still doubt as to the ability of bivalves to metabolize petroleum (Vandermeulen and Penrose, 1978). Thus, source fingerprints of oil may be rapidly altered once assimilated (i.e., transported across cell membranes) in organisms such as penaeid shrimp. Instead of being found in tissues as assimilated hydrocarbon residues, oil may actually exist as metabolic intermediates (i.e., oxygenated derivatives). The analytical tools to examine such metabolites are under development and are the subjects of active basic research (Malins et al., 1980).

While hydrocarbons may remain bound in the sediments for long periods of time (Blumer and Sass, 1972a,b; Johnston, 1970; Atlas et al., 1981), their availability to benthic organisms may vary. Even though a marine polychaete worm, Neanthes arenaceodentata, was observed to ingest naphthalene-contaminated sediments and to pass them through its digestive tract, average accumulation was less than 0.1 ppm total naphthalene after 38 days (Rossi, 1977). Anderson (1977) obtained similar results with the marine sipunculid, Phascolosoma agassizii. Capitella capitata, a polychaete that is sensitive to hydrocarbons in acute tests, was abundant in petroleum-affected sediments (Rossi et al., 1976). When a clam, Rangia cuneata, was introduced into contaminated sediments, the accumulation of naphthalenes in its tissues correlated closely with the sediment naphthalene concentrations (Fucik et al., 1977). Conversely, Roesijadi et al. (1978) found that the detrivorous clam Macoma inguinata was apparently unable to accumulate naphthalenes directly from contaminated sediments. Field studies of Shaw et al. (1976) produced significant mortalities to Macoma balthica when 5 µl oil/cm was applied to the surface sediment.

Selective uptake of petroleum components has been documented by Anderson et al. (1978), who have shown that uptake appears to be strongly related to a compound's release in a soluble form to the benthic boundary layer and its subsequent assimilation by benthic organisms. However, heavily impacted substrate appears to promote assimilation of unfractionated oil by some benthic organisms (Boehm et al., 1982). The persistence of petroleum in animal tissues is dependent on the exposure history of petroleum to the affected organisms (e.g., Anderson et al., 1974; DiSalvo et al., 1975; Boehm and Quinn, 1977; Lee et al., 1970; Stegeman and Teal, 1973). The physical/chemical form of petroleum (dissolved versus sorbed), the duration of exposure of organisms to oiled substrate, and the absolute levels of petroleum in the sediment are the major factors in determining rates of uptake, depuration, metabolism, and the chemical composition of the assimilated hydrocarbons.

Thus the uptake of oil by benthic crustacea, e.g., shrimp, is a complex function of the nature of the oil in the substrate, the level of exposure, and the organism's behavior. We cannot a priori expect to find whole Ixtoc I oil within these organisms unless they were contaminated during capture or have encountered large concentrations of undegraded oil. The analytical focus of a damage assessment program, therefore, should be on both the absolute levels of total hydrocarbons and the presence of petroleum-derived

aromatic hydrocarbons in tissues, the latter of which may be the most sensitive and relevant measurements of recent petroleum uptake. Giam et al. (1980) did not detect aromatic hydrocarbons in STOCS shrimp samples, so any significant hydrocarbons detected during the damage assessment study could be related to Ixtoc or Burmah Agate oils.

Hydrocarbons from a variety of sources are found in environmental samples. For purposes of discussing the results of this study we define the following terms:

1. Biogenic hydrocarbons - those compounds synthesized by marine and terrestrial organisms.

2. Anthropogenic inputs - any one of several sources of pollutant hydrocarbons originating from man's activities.

3. Chronic inputs - including the subcategories chronic petroleum inputs and pyrogenic inputs. The petroleum sources originate in land drainage, stormwater runoff, ballast water discharges, platform operations and more or less are considered continuous. Pyrogenic sources include the residues of fossil fuel (oil, coal, wood) combustion and enter the marine environment via urban air fallout and subsequent runoff.

4. Acute, episodic or spill related inputs - accidental releases, for purposes of this study those relating to Ixtoc I, Burmah Agate or other identifiable spill sources.

2.2 Methods and Approaches

The proper utilization and blending of different analytical techniques is the key to successful chemical assessment programs. The analytical techniques used in this program were (1) ultraviolet fluorescence spectroscopy (UV/F), (2) high resolution (fused silica) capillary gas chromatography (FSCGC) with flame ionization detection (FID) and sulfur-specific (Hall Electrolytic Conductivity) detection, (3) computer-assisted gas chromatographic mass spectrometry (GC/MS), and (4) stable isotope mass spectrometry.

A hierarchical analytical scheme beginning by screening large numbers of samples for the possible presence of oil using a "molecular property" measurement such as UV/F, and building in analytical complexity as needed, was developed for examining the molecular and atomic properties of hydrocarbons in the samples (Figure 2-2). As applied to the various sample types the detailed hierarchy shown in Figure 2-3 was utilized.

Because the main purpose in analyzing a series of oils and tar samples was to examine detailed molecular and atomic (isotopic) compositions of a variety of weathered oil samples in order to establish the range of source fingerprints, screening by UV/F was not required. Samples were selected

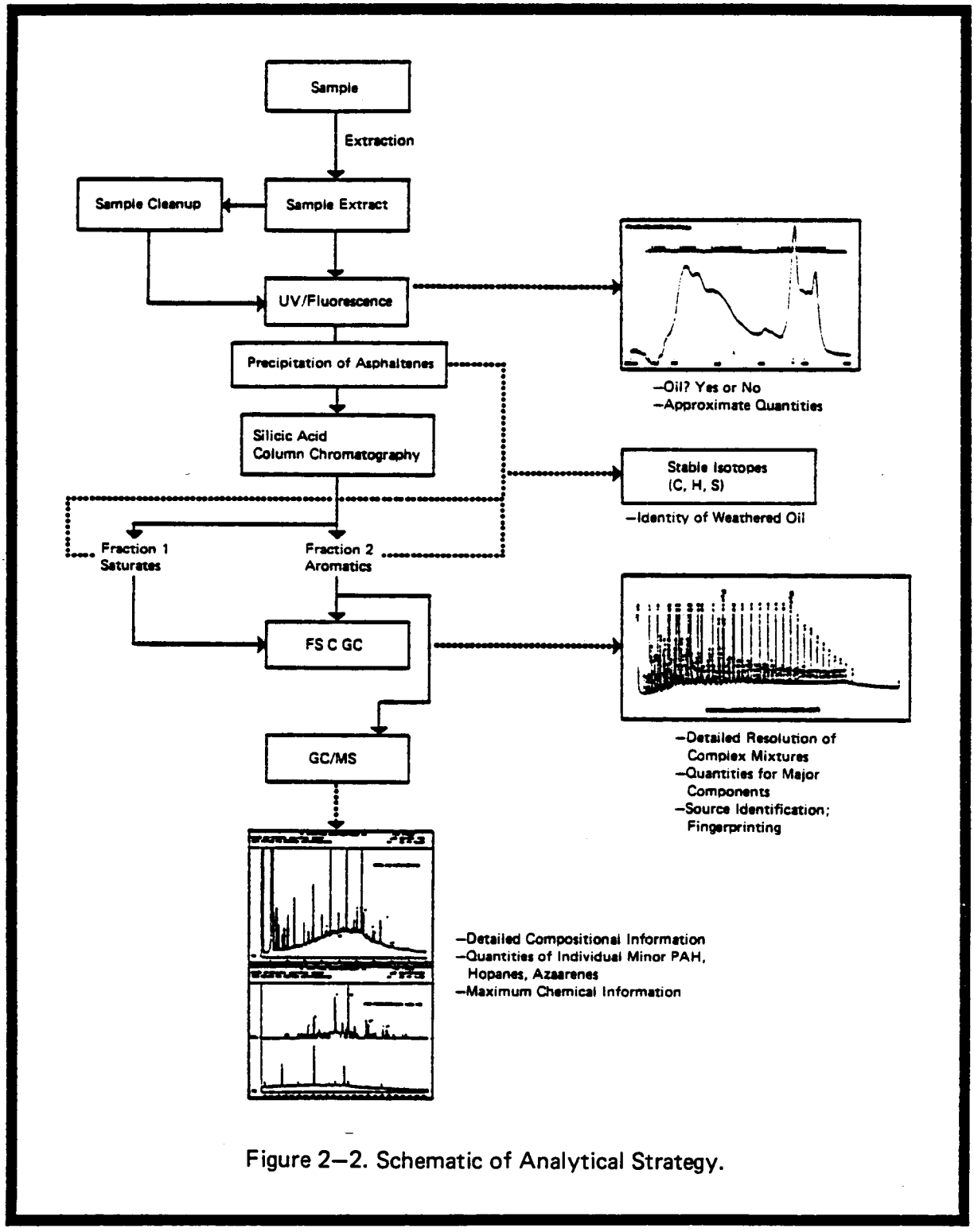


Figure 2–2. Schematic of Analytical Strategy.

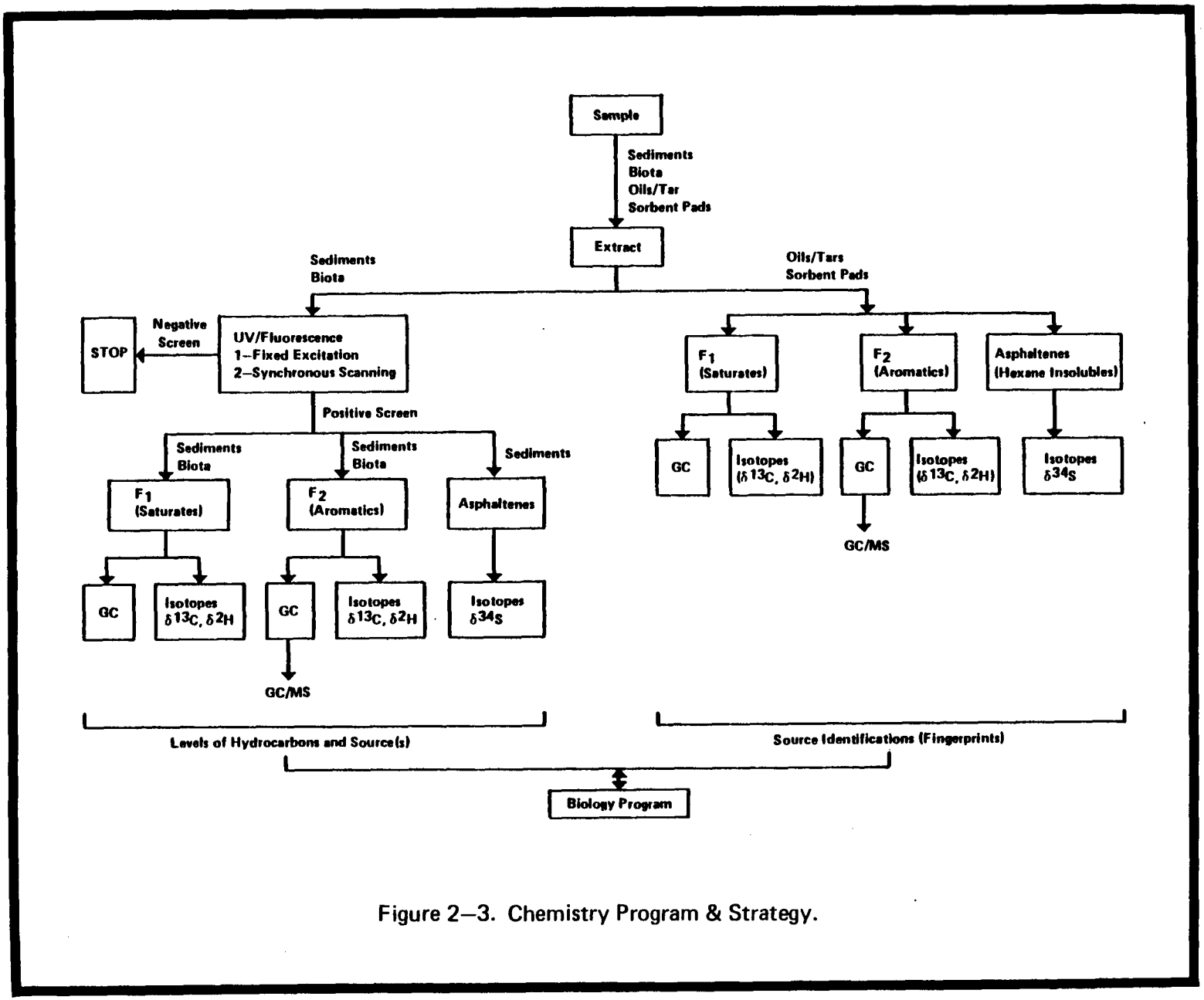


Figure 2–3. Chemistry Program & Strategy.

and subjected to FSCGC (FID) analysis to establish n-alkane patterns, FSCGC (Hall sulfur) to establish organic-sulfur component patterns, GC/MS to establish detailed aromatic hydrocarbon profiles, and stable isotopic analysis ($\delta^{13}C$,$\delta^{34}S$, δD; see Section 3) to examine atomic compositions.

Sediment and tissue samples, on the other hand, were all screened for the presence of oil by UV/F. Those positively screened were then further fractionated and subjected to FSCGC (FID), through which PHC quantification and compositional fingerprinting was achieved. Some samples were then subjected to GC/MS for aromatic identifications and quantifications, and to stable isotope determinations.

The analytical schemes for each sample type were designed to facilitate definitive, match-no match conclusions regarding a sample's PHC assemblage with a specific source through use of three major techniques - alkane matching (FSCGC), aromatic matching (GC/MS), and isotopic matching ($\delta^{13}C$, δD, $\delta^{34}S$). No one technique could have achieved definitive matching as at least two definitive matches are needed to establish probable identity.

The differences between this marine damage assessment analytical strategy and that used forensically by the Coast Guard (USCG, 1977), is that highly weathered oils are being considered in this study, as opposed to the USCG procedures, which apply to lightly and moderately weathered oils.

2.2.1 Sampling

Three sets of samples and/or data collected from the South Texas Outer Continental Shelf were potentially available for the Ixtoc I oil spill assessment. These sets were BLM-STOCS (1974-1977), RRT (1979), and BLM (1980). The BLM-STOCS Benchmark Study obtained baseline concentrations of petroleum in sediments and samples collected from 1974 to 1977. These samples were collected from 12 primary stations (Figure 2-4, Table 2-1). Data from this program were available on a set of NODC data tapes.

The regional response team and other groups, such as the NOAA Researcher/Pierce team, collected samples from July to December 1979 during the blowout event. Sediment, shrimp, and sorbent pad samples were collected from sites that included the 12 primary stations and more than 90 secondary stations (Tables 2-2 and 2-3, Figure 2-5). Additional shrimp samples were collected at dockside from shrimp fishermen fishing in the study region. The sampling location was determined post facto by interviewing the shrimpers and is without a doubt less certain than for the other samples. Although exact sampling locations are given (Table 2-4), the samples were given station numbers according to latitude and longitude quadrants (Figure 2-4). Beached oil samples were collected by a variety of individuals from a variety of stations (Table 2-5). Station numbers were assigned to identify a set of samples collected by one individual.

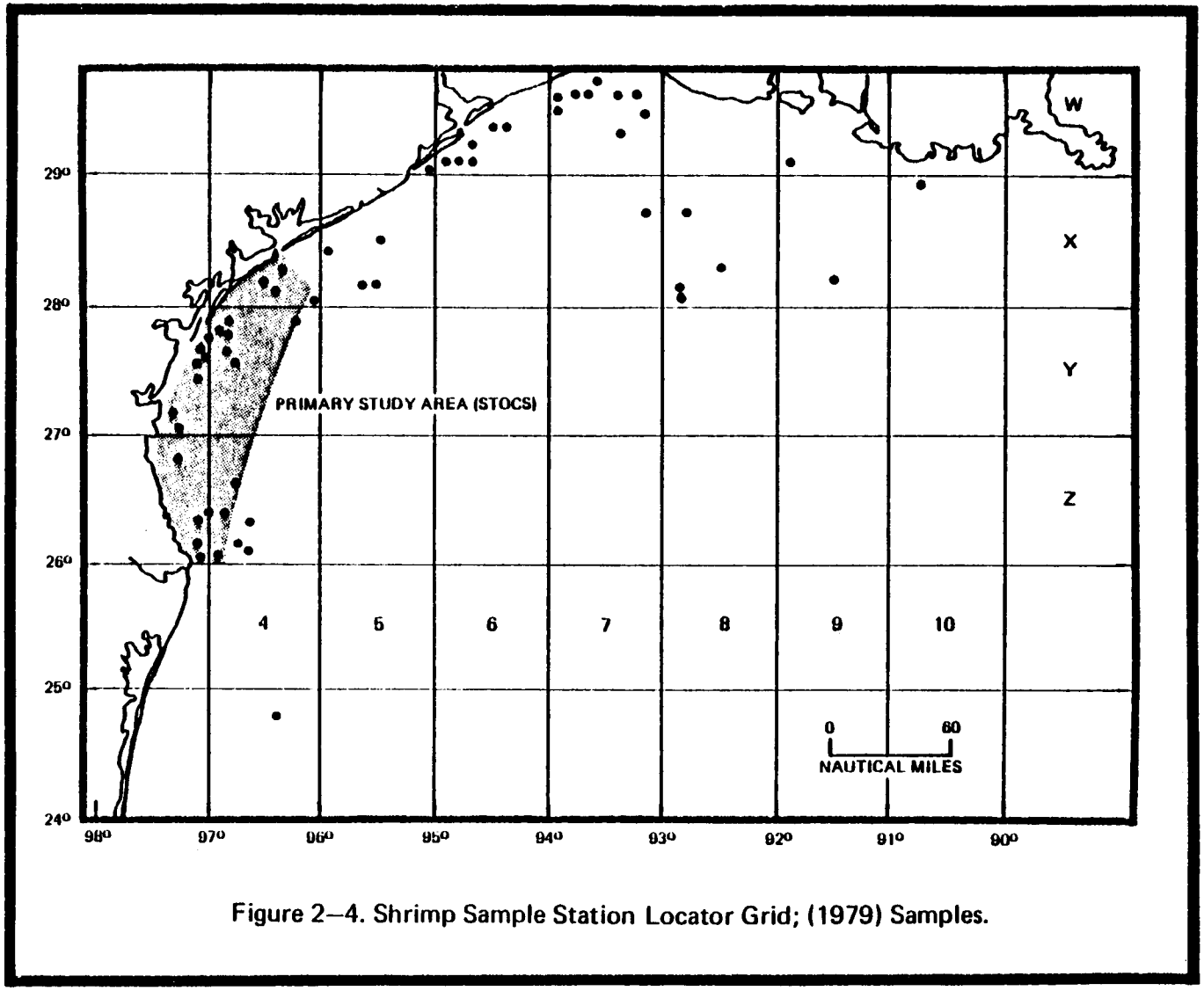


Figure 2–4. Shrimp Sample Station Locator Grid; (1979) Samples.

TABLE 2-1

LOCATION OF SAMPLING STATIONS: STOCS STATIONS[a]

STATION	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
N38 (I-1)	28°12'00"	96°27'00"	18
N39 (I-2)	27°55'00"	96°20'00"	42
N40 (I-4)	28°14'00"	96°29'00"	10
M35 (II-1)	27°40'00"	96°59'00"	22
M36 (II-2)	27°30'00"	96°45'00"	49
M37 (II-4)	27°34'00"	96°50'00"	36
S49 (III-1)	26°58'00"	97°11'00"	25
S50 (III-4)	26°58'00"	97°20'00"	15
S51 (III-5)	26°58'00"	97°02'00"	40
S52 (IV-1)	26°10'00"	97°01'00"	27
S53 (IV-4)	26°10'00"	97°08'00"	15
S54 (IV-5)	26°10'00"	96°54'00"	37

[a]Station numbers conform to the Ixtoc I Damage Assessment Team classification. "S" station numbers are farther south; "N" station numbers are farther north in the study area.

TABLE 2-2

LOCATION OF SAMPLING STATIONS:
REGIONAL RESPONSE TEAM SAMPLING STATIONS (PART 1)

STATION[a]	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
S04	26°39'12"	96°48'48"	55
S05	26°39'00"	97°00'00"	37
S15	26°03'12"	97°08'00"	9
S18	26°19'24"	97°05'30"	18
S21	26°23'30"	97°12'30"	9
S26	26°38'30"	97°12'24"	18
S27	26°38'12"	97°17'12"	9
S31	26°47'54"	97°20'12"	9
S43	26°23'30"	97°12'42"	4.5
S46	26°10'00"	97°09'48"	4.5
M14	27°18'18"	97°15'00"	18
M15	27°18'18"	97°19'42"	9
M21	27°32'24"	97°13'30"	9
M04	27°17'00"	96°48'42"	55
M05	27°17'12"	96°59'00"	37
M24	27°40'48"	97°02'24"	18
M25	27°41'24"	97°08'12"	9
M26	27°41'24"	97°08'30"	4.5
M28	27°32'24"	97°13'54"	4.5
N03	27°41'12"	96°30'30"	55
N04	27°49'00"	96°33'42"	37
N09	28°16'18"	96°28'18"	9
N18	28°00'00"	96°43'24"	18
N19	28°01'54"	96°51'30"	9
N32	28°02'12"	96°51'48"	4.5
N37	28°17'30"	96°28'42"	4.5

[a]All stations were sampled during December 1980 cruise.

TABLE 2-3

LOCATION OF SAMPLING STATIONS: RRT (PART 2)

STATION	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
R15	25°05'00"	95°43'00"	126
R16	25°07'00"	96°48'00"	85
R17	25°09'00"	96°54'00"	64
R18	25°11'00"	97°00'00"	50
R19	25°14'00"	97°07'00"	39
R20	25°15'00"	97°15'00"	25
R21	25°17'00"	97°17'00"	18
R23	25°58'00"	97°09'00"	23
R24	26°10'00"	97°00'00"	23
R25	26°10'00"	96°54'00"	37
R26	26°10'00"	96°39'00"	49
R27	26°10'00"	96°31'00"	61
R28	26°10'00"	96°24'00"	86
R30	27°18'00"	96°10'00"	-
ANA	29°13'00"	94°30'00"	-
ANB	28°40'00"	94°21'12"	-
ANC	27°47'30"	94°54'20"	-
AND	28°16'06"	94°58'00"	-
ANE	28°36'00"	95°42'48"	-
S01	26°58'00"	96°53'18"	55
S06	26°29'18"	96°57'24"	37
S9B	26°13'12"	96°33'36"	58
S12	25°58'42	97°05'00"	18
S13	25°58'00"	97°07'12"	9
S14	26°04'12"	97°05'30"	18
S16	26°14'00"	97°04'18"	18
S17	26°13'00"	97°09'48"	9
S19	26°18'30"	97°11'00"	9
S22	26°28'54"	97°08'42"	18
S23	26°28'18"	97°13'42"	9
S25	26°33'30"	97°15'24"	9
S29	26°43'00"	97°18'46"	9
S30	26°47'48"	97°16'12"	18
S33	26°52'54"	97°20'54"	5
S34	26°58'00"	97°17'20"	18
S47	26°03'12"	97°08'30"	5
S48	25°58'00"	97°08'06"	5

TABLE 2-3 (CONT.)

STATION	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
M09	27°03'12"	97°22'00"	9
M10	27°08'18"	97°17'24"	18
M11	27°08'18"	97°21'18"	9
M14	27°18'18"	97°15'00"	18
M15	27°18'18"	97°19'42"	9
M17	27°23'00"	97°19'48"	9
M19	27°27'54"	97°16'00"	9
M20	27°32'12"	97°08'24"	18
M21	27°32'24"	97°13'30"	9
M23	27°36'54"	97°10'30"	9
M31	27°18'18"	97°19'48"	5
M33	27°08'18"	97°21'42"	5
N27	27°45'48"	97°05'00"	9
N26	27°45'00"	96°59'00"	18
N11	28°14'42"	96°33'42"	9
N13	28°11'24"	96°38'12"	9
N15	28°08'12"	96°42'30"	9
N17	28°05'00"	96°46'42"	9
N20	27°56'12"	96°47'30"	18
N21	27°58'18"	96°55'30"	9
N23	27°54'30"	96°59'00"	9
N25	27°50'00"	97°01'30"	9
PA1	28°50'00"	97°02'00"	16
PA2	27°50'24"	97°03'12"	16
PA3	27°50'30"	97°03'54"	16
PA4	27°50'54"	97°03'54"	7
PA5	27°51'12"	97°03'24"	9

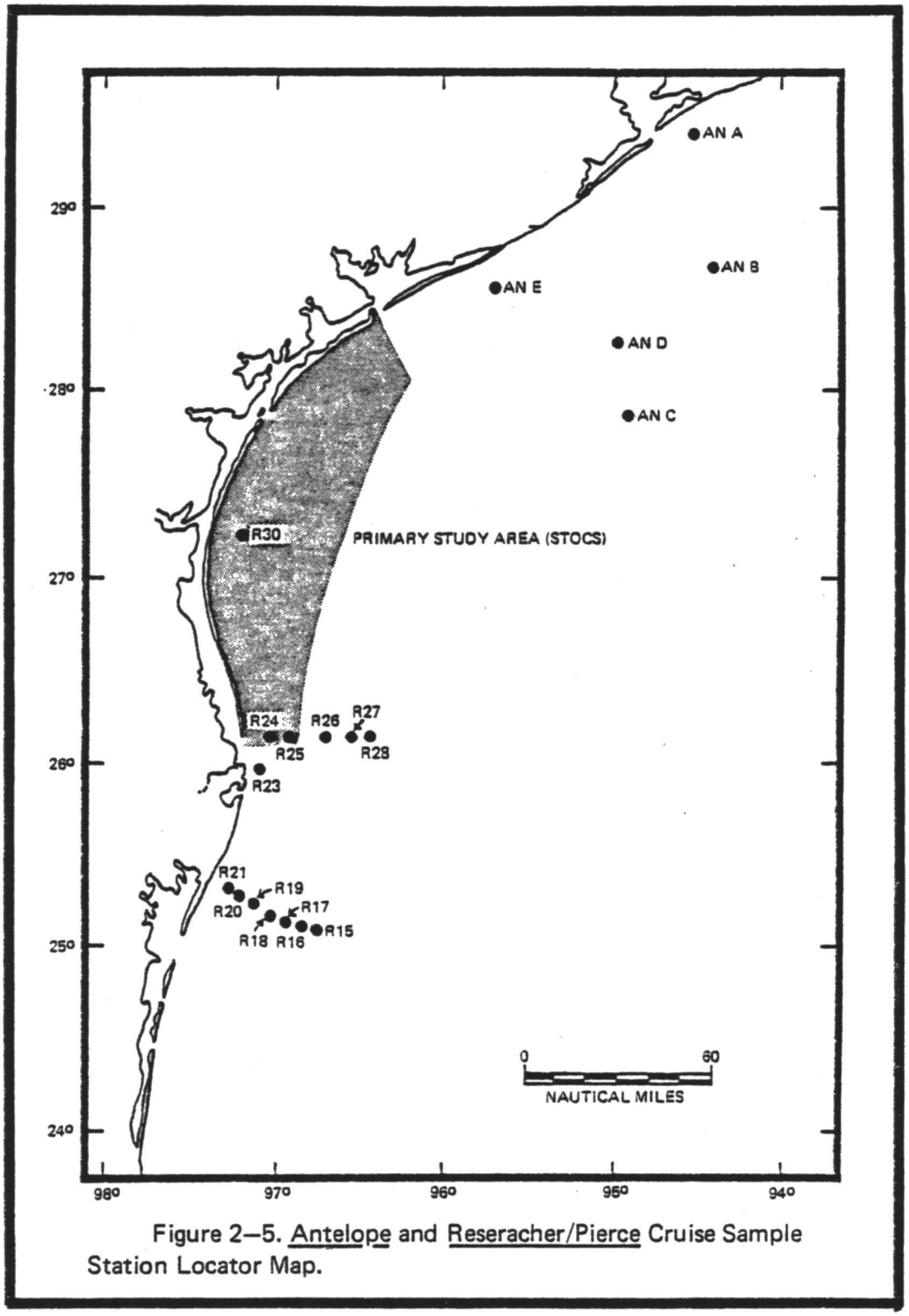


Figure 2–5. Antelope and Reseracher/Pierce Cruise Sample Station Locator Map.

TABLE 2-4

LOCATION OF SAMPLING STATIONS:
DOCKSIDE SHRIMP STATIONS

STATION[a]	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
W05	29°04'0"	95°05'0"	11
W06	29°30'0"	94°22'0"	9
	29°19'0"	94°16'0"	15
	29°34'0"	94°19'0"	4
	29°23'0"	94°34'0"	9
	29°11'0"	94°54'0"	9
	29°31'0"	94°06'0"	13
	29°30'0"	94°23'0"	13
	29°31'0"	94°06'0"	13
	29°12'0"	94°36'0"	11
	29°12'0"	94°47'0"	13
W07	29°37'0"	93°52'0"	7
	29°39'0"	93°44'0"	5
	29°43'0"	93°40'0"	5
	29°38'0"	93°44'0"	11
	29°42'0"	93°40'0"	7
	29°41'0"	93°13'0"	9
	29°34'0"	93°54'0"	9
W09	29°08'0"	91°57'0"	9
X01	29°49'0"	99°52'0"	9
X04	28°18'0"	96°30'0"	5
	28°25'0"	96°18'0"	57
	28°02'0"	96°03'0"	44
	28°11'0"	96°27'0"	7
X05	28°16'0"	95°32'0"	38
	28°16'0"	95°40'0"	33
	28°30'0"	95°57'0"	16
	28°30'0"	95°30'0"	27
X07	28°43'0"	93°05'0"	31
X08	28°24'0"	92°26'0"	40
	28°45'0"	92°44'0"	29
	28°13'0"	92°46'0"	69
Y03	27°34'0"	97°03'0"	26
	27°41'0"	97°01'0"	-
	27°39'0"	97°02'0"	-
	27°39'0"	97°02'0"	-
	27°45'0"	97°02'0"	-
	27°49'0"	97°00'0"	-
	27°49'0"	97°00'0"	-

TABLE 2-4 (CONT.)

STATION[a]	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
Y03	27°49'0"	97°00'0"	-
(Cont.)	27°45'0"	97°02'0"	-
	27°45'0"	97°02'0"	-
	27°43'0"	97°04'0"	-
	27°01'0"	97°11'0"	22
	27°12'0"	97°18'0"	16
Y04	27°50'0"	96°55'0"	-
	27°50'0"	96°55'0"	-
	27°50'0"	96°54'0"	18
	27°53'0"	96°51'0"	18
	27°50'0"	96°56'0"	18
	27°42'0"	96°42'0"	37
	27°55'0"	96°36'0"	37
	27°43'0"	96°51'0"	27
	27°43'0"	96°51'0"	9
Z03	26°11'0"	97°06'0"	18
	26°50'0"	97°14'0"	31
	26°04'0"	97°04'0"	24
	26°37'0"	97°00'0"	37
	26°34'0"	97°04'0"	-
	26°05'0"	97°04'0"	20
Z04	26°02'0"	96°57'0"	31
	26°08'0"	96°42'0"	46
	26°34'0"	96°57'0"	38
	26°08'0"	96°44'0"	44
	26°21'0"	96°38'0"	51

[a]Station names refer to latitude and longitude quadrants which are 1° squares. See Figure 2-3 for the location of the quadrants.

TABLE 2-5

LOCATION OF SAMPLING STATIONS: BEACHED OIL SAMPLES

STATION	LATITUDE (N)	LONGITUDE (W)	
T01	27°47'	97°04'	
T02	27°26'	97°17'	
T03	26°52'	97°23'	
T04	26°34'	97°17'	
T05	26°06'	97°10'	
T06	27°02'	97°22'	
Q01	26°04'	97°09'	
Q02	26°40'	97°28'	
Q03	26°04'	97°09'	
Q04	27°40'	97°10'	
Q05	28°05'	96°50'	
I5A	27°51'36"	97°03'05"	
I4C	27°43'48"	97°07'54"	
I03	26°41'00"	97°19'48"	
I17	26°24'42"	97°13'22"	
P01	25°57'45"	97°08'40"	
P02	26°23'25"	97°12'00"	
P06	26°14'40"	97°10'55"	
P09	26°24'50"	97°13'30"	
P10	26°33'40"	97°16'15"	
P12	27°36'40"	97°17'15"	
P17	27°02'05"	97°22'15"	
P19	27°32'05"	97°14'40"	
P20	27°40'30"	97°10'05"	
P24	27°42'25"	97°09'05"	
E01	—	—	
E02	—	—	
E03	—	—	
E04	—	—	
E05	—	—	
B01	—	—	South Big Shell
B02	—	—	Burmah Agate Area
B03	—	—	San Jose Island
B04	—	—	East Beach A
B05	—	—	PS NOAA 05
B06	—	—	Port Baker
B07	—	—	At NOAA 10
CM1	—	—	Malaquite
CM2	—	—	Malaquite

A third set of samples was collected by ERCO and LGL in December 1980 as part of this BLM study. Sediment and shrimp samples were collected from the 12 STOCS stations, 26 RRT stations, and 6 Burmah Agate stations (Table 2-6, Figure 2-6). In the interest of consistency, station names assigned by the RRT were employed whenever possible.

2.2.1.1 Cruise Description (December 1980)

The primary objective of this cruise was to collect a set of samples, the analysis of which will help determine the location(s) and impact of oil pollution from the Ixtoc I blowout off the Texas coast. Samples collected include surface sediment for petroleum hydrocarbon analysis, sediment for infaunal taxonomic population and diversity measurements, epifaunal (i.e., penaeid shrimp) organisms for petroleum hydrocarbon analysis, and possible shipboard contaminants for later reference. A secondary objective was to collect samples from the area of the Burmah Agate oil spill so that its impact on sediment geochemistry could be characterized. Field sampling efforts were conducted according to techniques used in the BLM STOCS Benchmark Study and employed to obtain collections aboard the R/V Longhorn during the RRT response in 1979.

The field sampling operations for the Ixtoc I oil spill assessment cruise were conducted from December 2 to 13, 1980 aboard F/V Tonya and Joe. The cruise departed Freeport, Texas at 1440 on December 2 and steamed south to occupy stations previously sampled by STOCS and RRT investigators. (See ERCO 1981 for details.)

2.2.1.2 Sampling Methods (December 1980)

To ensure compatibility, the same sampling gear used in the STOCS study was used for the December 1980 cruise.

At each station, a series of 10 sediment grabs were made using a Kahl Scientific, 0.1 m^2 stainless steel Smith-MacIntyre grab. From each of the first six grabs (biology grabs), three subsamples were removed - one each for taxonomy, grain size, and total organic carbon. From the last four grabs (chemistry grabs), a single pooled sample for hydrocarbon analysis was composited by removing a 250-g aliquot from each sample and placing it in a 1-litre Teflon jar.

Tissue sampling was conducted using a 20-ft otter trawl fitted with an uncoated nylon net and towing for 20 to 30 minutes at each station. The contents of each trawl were emptied into a stainless steel tray for sorting, and subsamples (3 to 20 individuals) of each species of shrimp were removed and frozen for subsequent analysis.

All navigation was performed using an EPSCO LORAN-C receiver fitted with an autoplotter for realtime conversion of time delays to latitude-longitude

TABLE 2-6

LOCATION OF SAMPLING STATIONS: BURMAH AGATE STATIONS

STATION	LATITUDE (N)	LONGITUDE (W)	DEPTH (m)
G01	29°17'48"	94°34'18"	12
G02	29°17'15"	94°38'00"	12
G03	29°08'00"	94°58'00"	10
G04	29°13'30"	94°42'00"	13
G05	29°12'00"	94°48'00"	12
G06	29°09'30"	94°53'30"	12

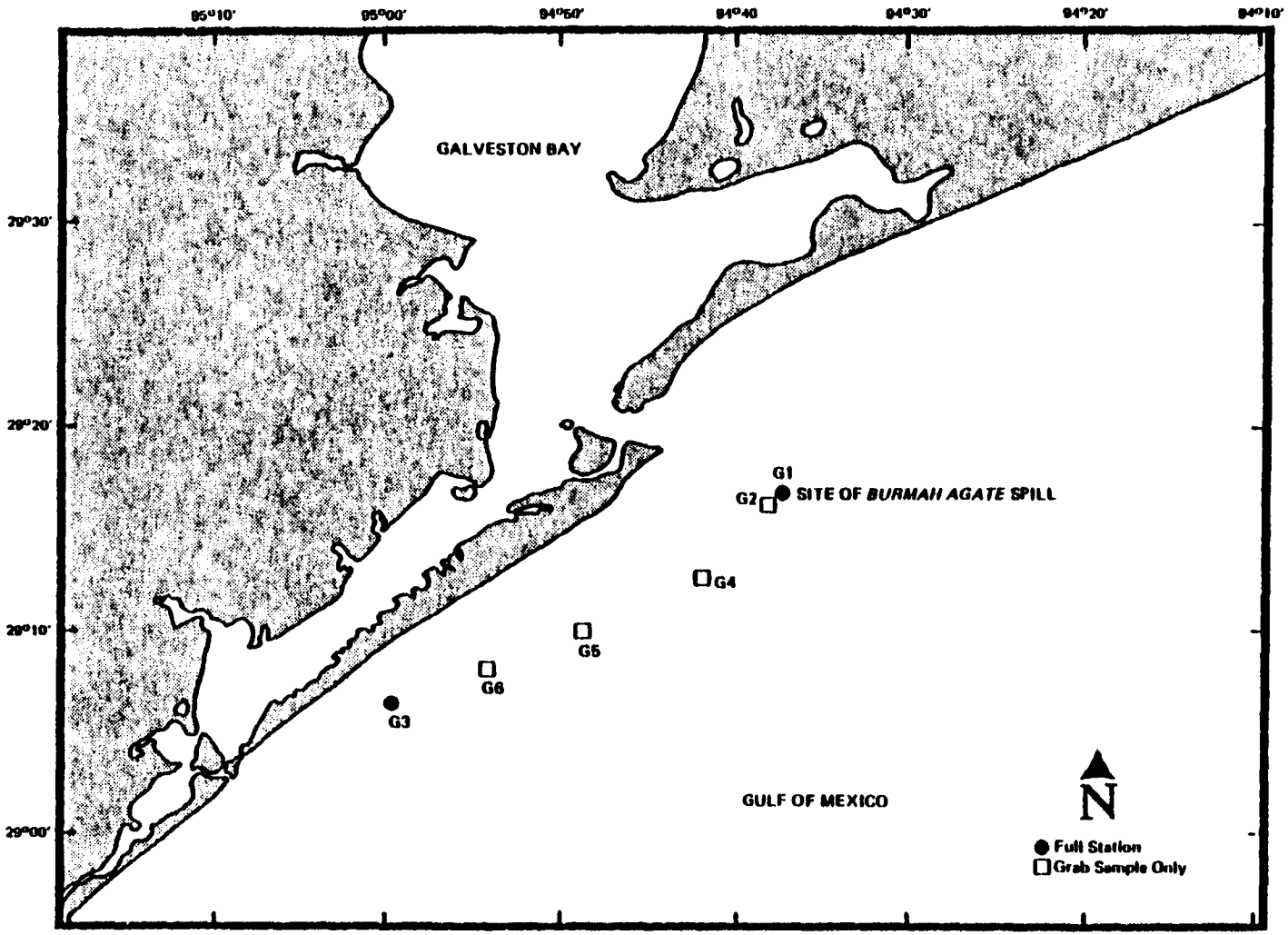


Figure 2–6. Burmah Agate Sampling Stations.

and display of ship track. Ship position was continuously monitored to ensure that all collections were made within a half-mile radius of station center.

To ensure that samples were not contaminated during collection, special precautions were taken during sampling operations. Subsampling of sediment grabs was performed with solvent-rinsed (methylene chloride) stainless steel utensils, and sediments were stored in solvent-rinsed Teflon jars. The stainless steel Smith-MacIntyre grab was washed with water from the vessel's seawater system between stations. A sample of this rinse water was collected as part of the shipboard contaminant sample set.

Tissue collections were made with an otter trawl equipped with an untarred nylon net. Trawl samples were emptied into a sea water- and solvent-rinsed stainless steel tray for sorting, and only solvent-rinsed utensils were used to handle specimens. Samples were stored in solvent-rinsed Teflon jars.

Shipboard samples were collected for subsequent analysis to determine potential contaminants resulting from vessel operations. These included samples of fuel oil, lube oil, bilge water, stack fallout, and seawater from the vessel's pumping system.

A summary of all samples collected during the Ixtoc I cruise in December 1980 is shown in Tables 2-7 and 2-8. A total of 797 samples were collected. A complete collection of 684 biological samples was obtained (228 for taxonomy, 228 for grain size, and 228 for total organic carbon). All pooled sediment samples (38) for hydrocarbon chemistry were obtained. Tissues could not be collected at one station (S27) but additional samples were collected at several stations where both brown and white shrimp were captured. Nine samples for quality assurance and contamination control were collected. Miscellaneous samples of opportunity (tar balls or anomalous sediments) were collected at several stations.

At the completion of the cruise, all taxonomic samples were released to LGL for subsequent analysis. All other samples were shipped to ERCO under the custody of Mr. David Fiest. At ERCO, an aliquot of each of the sediment samples was removed and placed in a solvent-rinsed glass jar for total organic carbon analysis.

2.2.1.3 Sample Collection Summary

A summary of all samples and data available to the Ixtoc I damage assessment is shown in Table 2-9 and in Appendix 9.1 (Table 9-12). Concentrations of petroleum hydrocarbons in samples collected during the STOCS study from 1974 to 1977 were obtained from data tapes; concentrations in samples collected during the RRT response and the 1980 BLM cruise were measured by ERCO. Data for sediments and shrimp samples were available from all years; sorbent pad and oil samples were only collected during the damage assessment study.

TABLE 2-7

SAMPLE SUMMARY - IXTOC OIL SPILL ASSESSMENT CRUISE (DECEMBER 1980)

SAMPLE TYPE	NUMBER OF SAMPLES COLLECTED		
	ACTUAL	PLANNED	PERCENT
1. Biological Samples			
Taxonomy	228	228	100
Grain Size	228	228	100
Total Organic Carbon	228	228	100
2. Chemical Samples			
Pooled Sediment	38	38	100
Tissues	41	38	111
White shrimp (*Penaeus setiferus*)	27		
Brown shrimp (*P. aztecus*)	13		
Unidentified	1		
Quality Assurance	10 (∿25 kg)	10 (∿25 kg)	100
3. Contamination Control Samples			
Fuel	2	2	100
Bilge Water	2	2	100
Lube Oil	2	2	100
Stack Fallout	1	0	-
Seawater Washdown System	2	0	-
4. Miscellaneous Samples			
Tarballs	13	0	-
Extra Sediments	2	0	-
Total	797		

TABLE 2-8

SAMPLE SUMMARY - BURMAH AGATE ASSESSMENT (DECEMBER 1980)

SAMPLE TYPE	NUMBER OF SAMPLES COLLECTED		
	ACTUAL	PLANNED	PERCENT
1. Biological Samples			
Taxonomy	12	12	100
Grain Size	12	12	100
Total Organic Carbon	12	12	100
2. Chemical Samples			
Hydrocarbons	6	6	100
Tissues	2	2	100
White shrimp (Penaeus setiferus)	1		
Brown shirimp (P. aztecus)	1		
Total	44		

TABLE 2-9

SAMPLE AND DATA COLLECTION SUMMARY:
IXTOC DAMAGE ASSESSMENT

YEAR	SOURCE	NUMBER OF SAMPLES			
		SEDIMENTS	SHRIMP	SORBENT PADS	BEACHED OILS
1974	STOCS* Data (pre-spill)	0	6		
1975	STOCS* Data (pre-spill)	18	8		
1976	STOCS* Data (pre-spill)	82	12		
1977	STOCS* Data (pre-spill)	37	15		
1979	RRT Samples (mid-spill)	99	65	9	30
1980	BLM Cruise Samples (post-spill)	44	51	0	23

*STOCS data are from the 12 primary stations only.

2.2.2 Sample Analysis

The analytical strategy for the chemical assessment consisted of three levels (Figure 2-2). In the first level, samples were extracted and analyzed by ultraviolet spectrofluorometry (UV/F) to screen them for the presence of petroleum. Those samples either suspected of containing petroleum or of interest due to time and position of the sampling were carried through to the next level, fused silica glass capillary gas chromatography flame ionization detection (FSCGC) and stable isotope analysis. These techniques were used to distinguish petroleum hydrocarbons from biogenic hydrocarbons and to identify the source of petroleum. Confirmation of the identity of the oil and measurement of low levels of aromatic hydrocarbons were both accomplished during the third phase when computer-assisted gas-chromatographic/mass spectrometry (GC/MS) was used. Additionally, capillary gas chromatography with sulfur-specific detection (Hall conductivity detector - S mode) was used to focus on the organic sulfur compounds. Nitrogen heterocyclic compounds were determined on a selected set of samples using gas chromatography/flame ionization detection (GC/FID) of the nitrogen compounds, following acidic extraction of the organic extract.

Four types of samples - sediments, tissues, beached oils, and sorbent pads - were analyzed within this study, each according to a slightly different analysis scheme. Each sample type required a unique initial processing/sample extraction protocol and followed its own analytical decision tree. Sorbent pads and oil samples contained oil and were immediately analyzed by Level 2 techniques, FSCGC and stable isotope analysis, without a Level 1 screening (Figure 2-7). Shrimp and sediment samples were first analyzed by the Level 1 technique, UV/F, and subsequently analyzed by Level 2 and Level 3 methods (Figures 2-8 and 2-9). Each step of the hierarchical analytical scheme is discussed below.

2.2.2.1 Sample Processing

The initial step of the chemical analysis was to extract the petroleum hydrocarbons from the sample matrix. This process was unique for the oils, sorbent pads, shrimp, and sediments. Subsequent analytical steps were nearly identical for all samples.

Oils

Two types of oil samples were received:. tar and heavily oiled beach sediments. An aliquot of each tar sample was removed with a metal spatula, dissolved in dichloromethane, and dried using sodium sulfate. A measured aliquot (5 percent) of the dichloromethane (Baker resianalyzed) was weighed on a Cahn Model 26 electrobalance to determine the total lipid concentration.

One aliquot of the dichloromethane extract was removed to isolate the asphaltenes for stable isotope analysis. The volume of dichloromethane solvent containing about one gram of oil was transferred to a 50-ml centrifuge

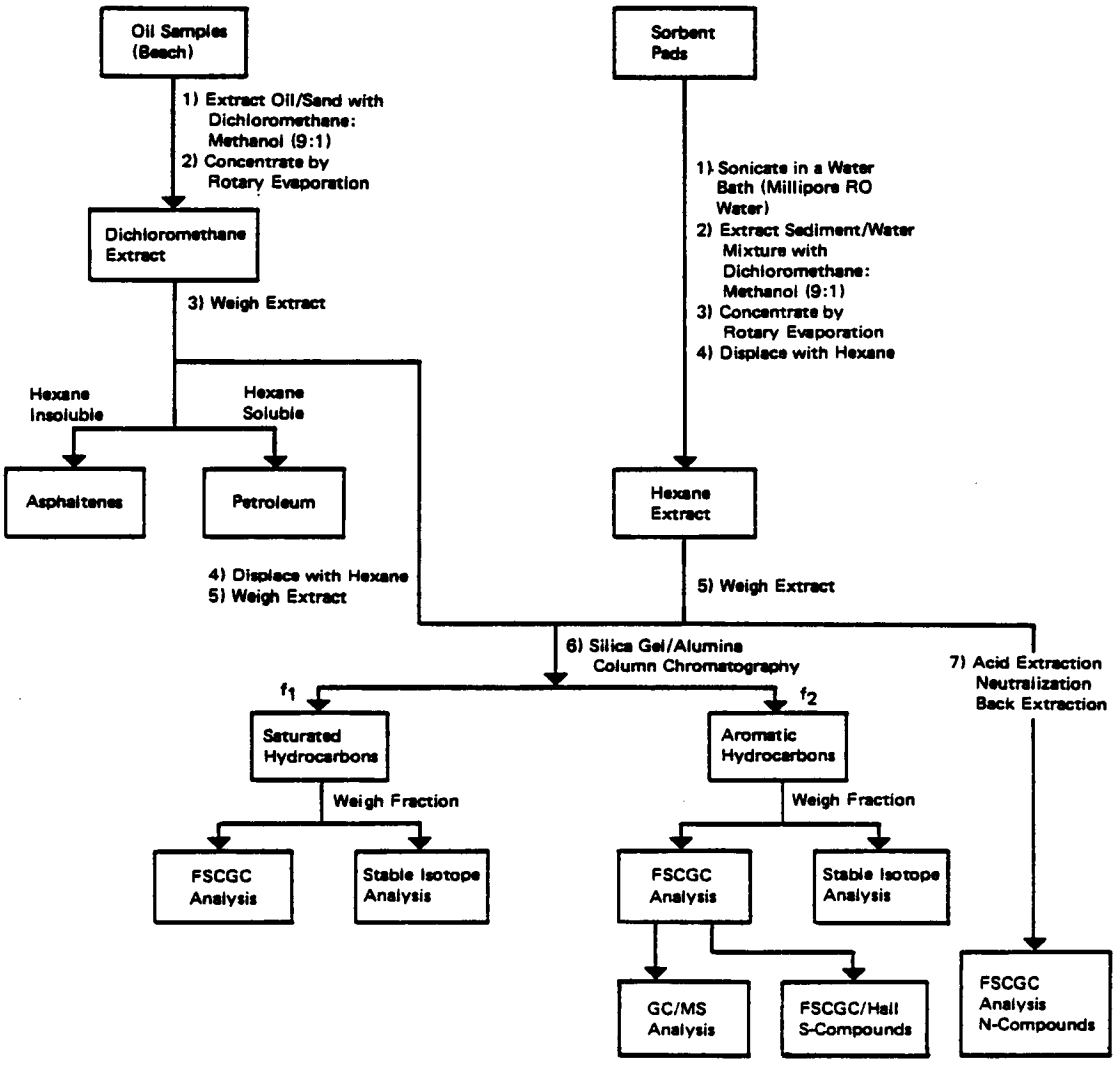


Figure 2–7. Analytical Scheme for Hydrocarbon Analysis for Sorbent Pads and Oil Samples.

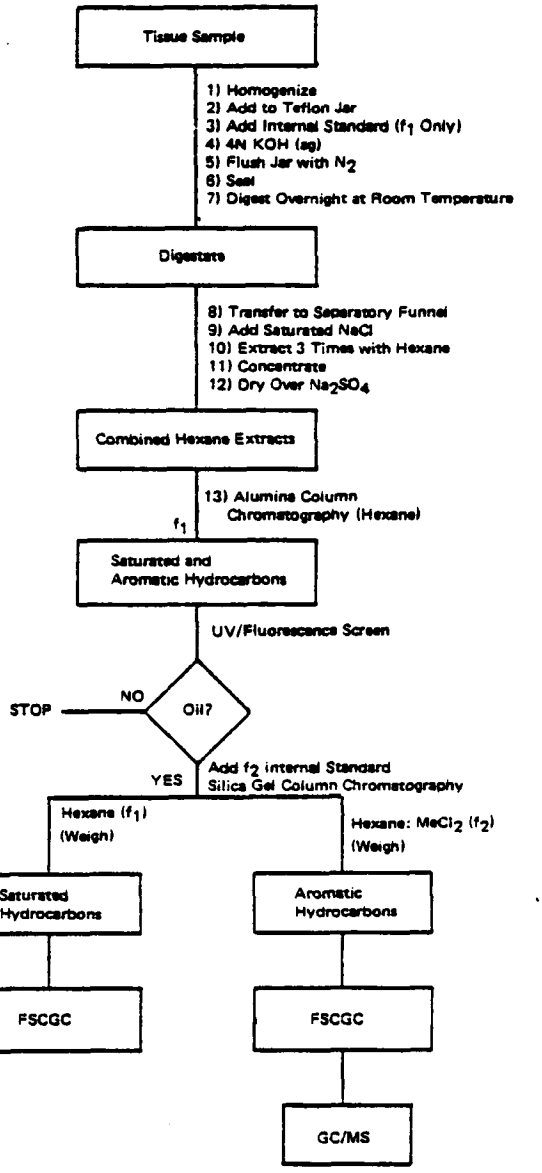


Figure 2–8. Analytical Scheme for Tissue Samples (from Warner, 1976; Boehm et al., 1982).

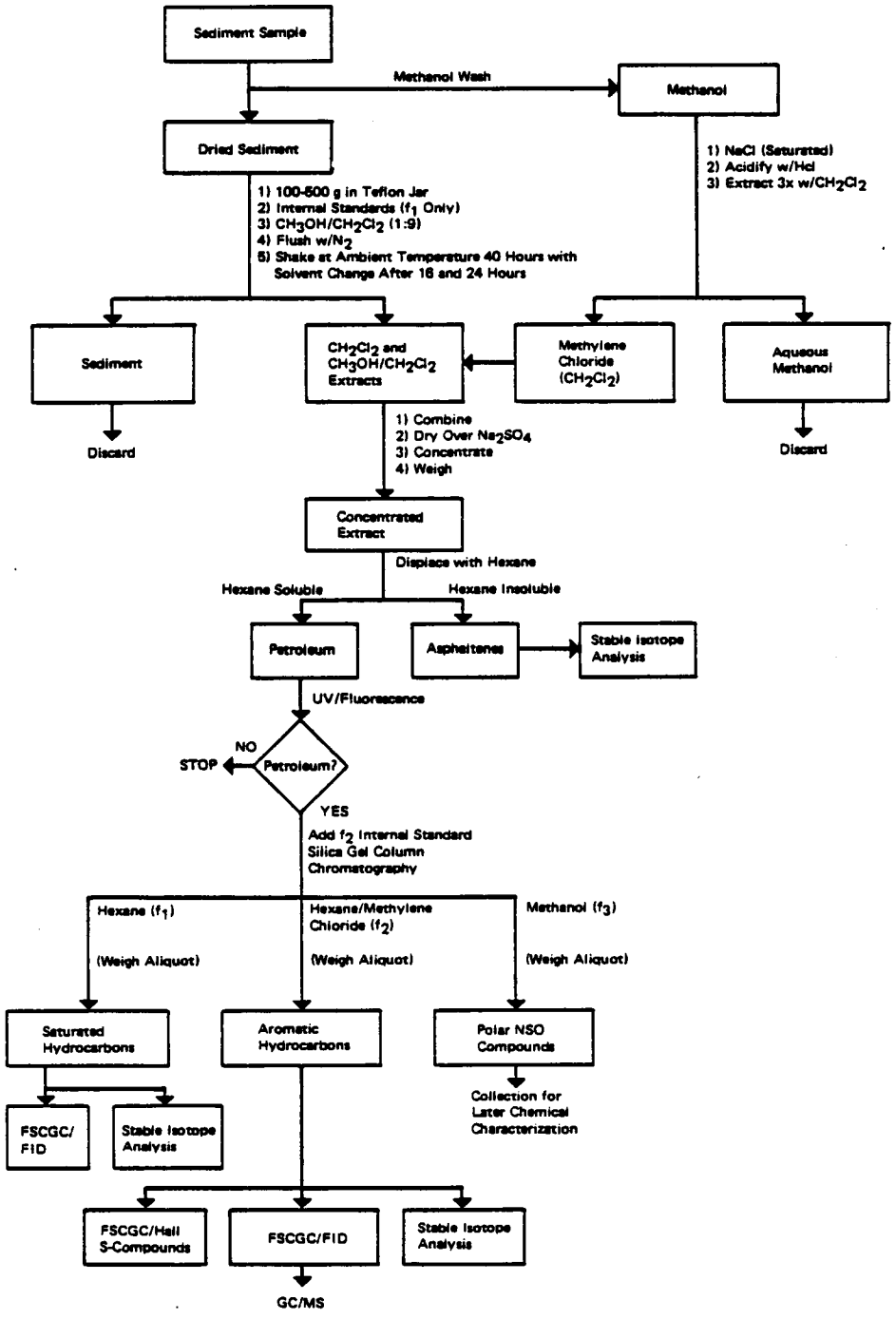


Figure 2–9. Analytical Scheme for Sediment Samples.

tube and concentrated to less than 1 ml under a stream of nitrogen. Thirty ml of hexane were added to precipitate the asphaltenes, which were isolated by centrifugation. The asphaltenes were washed with an additional 30 ml of hexane, then redissolved in dichloromethane.

A second aliquot of the dichloromethane extract was spiked with 10 μg each of androstane and d_{10}-phenanthrene and fractionated by silica gel/alumina column chromatography, after which each of the resulting saturated and aromatic hydrocarbon fractions was analyzed by FSCGC. The fractionation and FSCGC procedures are described in subsequent sections (2.2.2.3 and 2.2.2.4). Selected samples were analyzed by GC/MS and GC/Hall sulfur techniques (see Sections 2.2.2.5 and 2.2.2.6).

The concentrated extract was fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions, which were analyzed by an FSCGC (see Sections 2.2.2.3 and 2.2.2.4). The aromatic fractions of selected samples were analyzed by GC/MS (see Section 2.2.2.5).

Shrimp

Frozen shrimp samples were received in sealed glass jars. The species of the shrimp in the sample was confirmed by observing markings and shell characteristics.

The extraction and analytical procedure was based closely on that of Warner (1976) as revised by Boehm et al. (1982). The extraction and separation procedure follows.

Fifty to one hundred g (wet) of penaeid shrimp (a minimum of 12 individuals) were shelled, deheaded and minced with a sharp knife. A small aliquot of the tissue homogenate was taken for wet weight/dry weight determination. The remaining sample was transferred to a Teflon jar, and 50 ml of 4N KOH(aq) and 50 ml of methanol were added. Only a saturated internal standard (10 µg of androstane) was added at this time so as not to interfere with UV/F determinations. The mixture was flushed with nitrogen, sealed and allowed to digest at 60° C for 4 hr. The mixture was then transferred to a separatory funnel and extracted three times with 50 ml of hexane. The hexane was dried with sodium sulfate, concentrated, charged to an alumina cleanup column (12 g of 5% deactivated alumina), and eluted with 30 ml of dichloromethane. The dichloromethane was concentrated, displaced with hexane, charged to an alumina chromatography column (6.5 g of 7.5% deactivated alumina; 2 g Na_2SO_4) and eluted with 25 ml of hexane. The fraction was concentrated to 1 ml by rotary evaporation, at which time the extract was ready for UV/F analysis.

All extracts were analyzed by Level 1 UV/F (see Section 2.2.2.2). Selected samples were then fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions which were analyzed by FSCGC (see Sections 2.2.2.3 and 2.2.2.4). The aromatic fractions of some of these samples were also analyzed by GC/MS (see Section 2.2.2.5) and/or FSCGC (Hall detector - S mode) (see Section 2.2.2.6). Prior to FSCGC and GC/MS analyses of aromatic fractions d_{10}-phenanthrene was added as a quantification standard. Aromatic compound concentrations, thus dervied, were corrected for method recoveries (60-80%).

Sediments

Sediment samples were received in sealed glass jars and polyethylene bags. Preliminary experiments showed that water leaches of the polyethylene bags contained few and insignificant levels of interfering peaks when analyzed by UV/fluorescence and fused silica capillary gas chromatography.

The extraction method for the sediment samples was based on those of Brown et al. (1979) and Boehm et al. (1981b).

Approximately 100 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 100 ml of methanol. The methanol was transferred into a 500-ml separatory funnel containing 100 ml of water (Millipore RO), acidified to a pH of 2 with hydrochloric acid and extracted three times with 30 ml of dichloromethane. The dry sediment was then extracted three times with 100 ml of dichloromethane:methanol (9:1) by shaking for a minimum of 8 hr for each extraction. Approximately 10 µg of androstane was added as an internal standard. All solvent extracts were combined, dried using sodium sulfate and concentrated to 1 ml by rotary evaporation.

At this point, the dichloromethane was displaced with hexane to precipitate any polar and asphaltic compounds. The hexane was decanted and analyzed by UV/F (see Section 2.2.2.2), and the asphaltenes were redissolved in dichloromethane and stored at 4° C awaiting stable isotope analysis. Selected samples were fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions, which were analyzed by FSCGC (see Sections 2.2.2.3 and 2.2.2.4) and stable isotope analysis (see Section 3.2). The aromatic fractions of some of these samples were analyzed by GC/MS (see Section 2.2.2.5). D_{10}-phenanthrene was added as a quantification standard prior to FSCGC and GC/MS analyses. Another subset of samples was analyzed by FSCGC (Hall-S-mode) to examine the organo-sulfur compound composition of the sediments (see Section 2.2.2.6).

2.2.2.2 UV Fluorescence Analysis

Although fixed excitation UV/fluorescence was called for in the original contract, the synchronous excitation/emission technique has been widely employed in recent years to examine the detailed fluorescent properties of environmental samples. The contract was modified to allow analysis of the shrimp and sediment samples by both fixed excitation and synchronous excitation/emission techniques. The purpose of the UV/F screening was to identify those samples containing elevated levels of petroleum suspected to be from the Ixtoc I blowout.

The fixed excitation technique was based on the method of the United States Coast Guard (1977). The sample was diluted to a working concentration range with hexane and transferred to a 10-mm square quartz cell for analysis. For the fixed excitation technique, the excitation monochromator was held at a constant wavelength (254 nm), while the emission monochrometer was scanned from 250 to 500 nm. Instrumental conditions are listed in Table 2-10.

The synchronous excitation technique was based on the methods of Wakeham (1977) and Gordon and Keizer (1974). A measured aliquot of the sample extract was dissolved in a known volume of hexane. The intensity of the

TABLE 2-10

UV SPECTROFLUOROMETRY ANALYTICAL CONDITIONS

Instrument:	Farrand Mark I spectrofluorometer	
Features:	Corrected excitation Corrected emission	
Slits:		
Excitation:	2.5 nm	
Emission:	5.0 nm	
Scan speed:	50 nm/min	
Cell:	10 mm quartz	
Monochrometers:	Synchronous	Fixed
Excitation:	225-475 nm	254 nm
Emission:	250-500 nm	250-500 nm
Daily calibration:	API No. 2 fuel oil	
Quantification:	External standard	

fluorescence emission was measured from 250 to 500 nm while synchronously scanning the excitation monochrometer at a wavelength 25 nm smaller than the wavelength of the emission monochrometer. This technique measures aromatic hydrocarbons with a two- to five-ring aromatic structure (Lloyd, 1971).

The intensities of the fluorescence spectra were measured at several wavelengths (Table 2-11), which correspond to peak maxima present in an Ixtoc I reference oil sample. The fluorescence spectra were converted to relative concentration units by comparing the peak height at each wavelength to that of the appropriate No. 2 fuel oil standard curve. No. 2 fuel oil was used as the calibration standard as it yields a very reproducible and widely available standard. Since the exact composition of the fluorescent material in the shrimp and sediment samples was not uniform and not known, a single suitable calibration standard such as Ixtoc I could not be used.

2.2.2.3 Fractionation

Those sediment and shrimp samples chosen for Level 2 analyses and all of the oil and sorbent pad samples were fractionated by silica gel/alumina column chromatography prior to fused silica capillary gas chromatography. Column chromatography isolated the saturated and aromatic hydrocarbons from the total extract, thereby facilitating the identification and quantification of individual hydrocarbon compounds which were present in the sample extract.

The procedure was that of Boehm et al. (1982) and is summarized below.

The total extract was charged to a 100% activated silica gel/5% deactivated alumina/activated copper (11 g, 1 g, 2 g) chromatography column that was wet-packed in dichloromethane and prepared by eluting with 30 ml each of dichloromethane and hexane. The column was eluted with 18 ml of hexane followed by 21 ml of hexane:dichloromethane (1:1) to isolate the saturated (f_1) and unsaturated (f_2) hydrocarbons, respectively. After concentrating each fraction by rotary evaporation, the total gravimetric concentration was determined by weighing a measured aliquot on a Cahn Model 26 electrobalance.

2.2.2.4 Fused Silica Capillary Gas Chromatography

Fused silica capillary gas chromatography (FSCGC) analysis served to identify and quantify the petroleum hydrocarbon compounds present in the sample. The relative concentrations of individual compounds served to fingerprint the type of oil present, and the absolute concentrations served as a measure of the amount of oil present. The concentrations of certain compounds were also used to calculate indicator ratios that reveal the type of hydrocarbons present, i.e., biogenic or petroleum, and the weathering age of the petroleum.

Each fraction was analyzed by fused silica capillary gas chromatography on a Hewlett Packard 5840 gas chromatograph equipped with a splitless injection

TABLE 2-11

UV SPECTROFLUOROMETRY DATA OUTPUTS

Synchronous Excitation:	
Wavelengths (nm):	310, 356, 400, 437
Concentration units:	$\mu g \cdot g^{-1}$ dry weight #2 fuel oil equivalents
Fixed Excitation:	
Wavelengths (nm):	320, 355, 400, 437
Concentration units:	$\mu g \cdot g^{-1}$ dry weight #2 fuel oil equivalents

port and a flame ionization detector. Wall Coated Open Tabular fused silica columns (0.25 mm x 30 m, J&W Scientific) coated with SE30 and SE52 stationary phase were used to analyze the f_1 and f_2 from the column chromatography respectively. The instrumental conditions are listed in Table 2-12. Compounds were identified by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane for the f_1, d_{10}-phenanthrene for the f_2). The total concentrations of saturated and aromatic hydrocarbons were determined by planimetering the unresolved area, converting it to integrator area units, adding it to the total resolved integrated area, and calculating a concentration using the internal standard method.

The analytical outputs from the FSCGC are listed in Tables 2-13, 2-14, and 2-15. The concentrations of n-alkanes and isoprenoids were reported on a dry weight basis. From these concentrations a series of key diagnostic parameters were calculated. These ratios are useful in establishing the source of the oil, the contribution of biogenic hydrocarbons, and the degree that the oil was weathered.

2.2.2.5 Gas Chromatography/Mass Spectrometry

Selected samples found to contain petroleum by the Level 2 analyses were analyzed by fused silica capillary gas chromatography/mass spectrometry (GC/MS) to verify the source of petroleum or to identify the petroleum source in samples for which the n-alkane fingerprint was weathered and therefore inconclusive. The concentrations of a series of polynuclear aromatic hydrocarbons, in particular the alkylated phenanthrenes and dibenzothiophenes, serve as a fingerprint of weathered petroleum.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography (see Section 2.2.2.3) was analyzed for polynuclear aromatic hydrocarbons by GC/MS. An aliquot of the fraction was analyzed using a Hewlett Packard 5985 instrument equipped with a 0.25 mm x 30 m SE52 fused silica capillary column (J&W Scientific), which was threaded directly into the ion source. Instrumental conditions are listed in Table 2-16.

Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices and suspected to be present in the samples. If necessary the mass spectrum and retention time of an identified peak was retrieved and compared with an authentic standard or to a mass spectrum library to aid in identification of the compound. An in-house probability-based computer matching system, the HP 7920 multi-disc system containing EPA/NIH probability-based mass spectral libraries, was utilized for this purpose.

Concentrations of the identified compounds were determined by measuring peak areas of the appropriate peaks in the selected ion chromatograms and relating them to that of the internal standard. Relative response factors

TABLE 2-12

FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/
FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS

Instrument:	Hewlett Packard 5840 gas chromatograph
Features:	Split/splitless capillary inlet system Microprocessor-controlled functions
Inlet:	Splitless
Detector:	Flame ionization
Column:	
f_1:	0.25 mm I.D. x 30 m SE30 fused silica (J&W Scientific)
f_2:	0.25 mm I.D. x 30 m SE52 fused silica (J&W Scientific)
Gases:	
Carrier:	Helium 2 ml/min
Make-up:	Helium 30 ml/min
Detector:	Air 240 ml/min
Temperatures:	
Injection port:	250° C
Detector:	300° C
Column oven:	40-290° C @ 3° C/min
Daily calibration:	Alkane/aromatic mixture
Quantification:	Internal standard (f_1 androstane, f_2 d_{10} phenanthrene)

TABLE 2-13

COMPOUNDS QUANTIFIED BY FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY

COMPOUND	ANALYTICAL TECHNIQUE	USE
Saturated hydrocarbons		
n-alkanes ($n-C_{10}$ to $n-C_{34}$)	Capillary GC	Weathering and source indicators, especially when ratios are derived
Isoprenoids (farnesane, pristane, phytane, 1650, 1380)	Capillary GC	Weathering indicator (marker compounds as a group in lightly weathered samples)

TABLE 2-14

FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY ANALYTICAL OUTPUTS
(KEY DIAGNOSTIC PARAMETERS)

VARIABLE	DEFINITION OR ABBREVIATION	UNITS
1. Sum of n-alkanes, C_{14}-C_{32}	N-alkanes (C14-C32)	$\mu g \cdot g^{-1}$
2. Pristane/phytane	Pr/Ph	-
3. Pristane/n-C_{17}	Pr/n-C17	-
4. Phytane/n-C_{18}	Ph/n-C18	-
5. (Pristane + phytane)/sum of n-alkanes		-
6. Sum of n-alkanes, C_{14} to C_{18}	SUM LOW	% of total n-alkanes
7. Sum of n-alkanes, C_{19} to C_{24}	SUM MID	% of total n-alkanes
8. Sum of n-alkanes, C_{25} to C_{32}	SUM HI	% of total n-alkanes
9. Average OEP of n-alkanes, C_{14} to C_{18}	OEP LOW	-
10. Average OEP of n-alkanes, C_{19} to C_{24}	OEP MID	-
11. Average OEP of n-alkanes, C_{25} to C_{32}	OEP HI	-
12. Average OEP of n-alkanes, C_{14} to C_{32}	AV. OEP	-
13. Average OEP of n-alkanes, C_{14} to C_{20}	OEP1	-
14. Average OEP of n-alkanes, C_{20} to C_{32}	OEP2	-
15. CPI of n-alkanes, C_{14} to C_{20}	CPI1	-
16. CPI of n-alkanes, C_{20} to C_{32}	CPI2	-
17. Alkane/isoprenoid ratio	ALK/ISO	-
18. Saturated hydrocarbon weathering ratio	SHWR	-
19. Aromatic weathering ratio (GC/MS)	AWR	-

TABLE 2-15

EXPLANATION OF PETROLEUM WEATHERING RATIOS

The Biodegradation Ratio (Alkane/Isoprenoid)

$$ALK/ISO_{14-18} = \frac{[1400] + [1500] + [1600] + [1700] + [1800]}{[1380] + [1470] + [1650] + [1708] + [1810]}$$

The ALK/ISO ratio approaches 0 as the n-alkanes are depleted.

The Saturated Hydrocarbon Weathering Ratio (SHWR)

$$SWHR = \frac{[\text{sum of n-alkanes from n-}C_{10} \text{ to n-}C_{25}]}{[\text{sum of n-alkanes from n-}C_{17} \text{ to n-}C_{25}]}$$

The SWHR approaches 1.0 as low-boiling saturated hydrocarbons (n-C_{10} to n-C_{17}) are lost by evaporation.

The Aromatic Weathering Ratio (AWR)

$$AWR = \frac{\text{Total naphthalenes + fluorenes + phenanthrenes + dibenzothiophenes}}{\text{Total phenanthrenes + dibenzothiophenes}}$$

The AWR approaches 1.0 as low-boiling aromatics are lost by evaporation and/or dissolution.

TABLE 2-16

GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS

INSTRUMENT:	Hewlett Packard 5985 gas chromatograph/mass spectrometer
FEATURES:	HP 5933 data system with 7900 and 7920 disc drives 5840 gas chromotograph
INLET:	Splitless
DETECTOR:	Mass spectrometer
SCAN RATE:	400 amu/sec (46-446 amu)
IONIZATION VOLTAGE:	70 eV
COLUMN:	0.25 mm i.d. x 30 m SE52 fused silica (J&W Scientific)
INTERFACE:	Direct insertion of column into source
CARRIER GAS:	Helium 2 ml/min
TEMPERATURES:	
INJECTION PORT:	250° C
TRANSFER LINE:	300° C
SOURCE:	250° C
GC OVEN:	40-290° C, 3° C/min (temperature program)
DAILY CALIBRATION:	PFTBA and DFTPP aromatic mixture
QUANTIFICATION:	Internal standard (d_{10}-phenanthrene) (response factors)

for each component were calculated from analyses of analytical standards, if available, or were extrapolated. The compounds reported from the GC/MS analyses are listed in Table 2-17.

2.2.2.6 Gas Chromatography/Hall Detector (Sulfur Mode)

Selected oil and sediment samples were analyzed by gas chromatography/ Hall detector (sulfur mode) to obtain a fingerprint of the sulfur compounds for petroleum source identification. The relative concentrations of a series of sulfur-containing polynuclear aromatic hydrocarbons were measured by this technique.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography (see Section 2.2.2.3) was analyzed for sulfur-containing aromatics by GC/Hall (sulfur mode). An aliquot of the fraction was analyzed using a Hewlett Packard 5850 gas chromatograph to which a Tracor 603 conductivity detector was coupled. The selector was operated in the sulfur mode. Compounds were identified by comparing the retention times of peaks in the sample with retention time of known compounds. Since the trace was used as a fingerprint, identification of every compound was not necessary and only relative concentrations were reported. A series of nine peaks corresponding to alkyldibenzothiophenes were reported.

2.2.2.7 Acid Extraction of Nitrogen-Containing Compounds

Selected oil samples were analyzed for nitrogen-containing aromatic compounds by using an acid extraction technique to isolate the compounds and FSCGC and GC/MS to identify the compounds.

The procedure for isolating the nitrogen-containing compounds was similar to that of Overton et al. (1980). In summary: an aliquot of the total extract of oil samples was dissolved in 20 ml of hexane and extracted three times with 20 ml of 3N hydrochloric acid. The acidic aqueous extract was back-extracted twice with 20 ml of hexane, made basic with 6N KOH and extracted three times with 20 ml each of dichloromethane. The combined dichloromethane extracts were dried with sodium sulfate, concentrated by rotary evaporation, and finally concentrated under a nitrogen stream. The extracts were analyzed by FSCGC and GC/MS using conditions described in Sections 2.2.2.4 and 2.2.2.5, respectively.

2.3 Results

The hydrocarbon compositions and concentrations of the environmental samples examined by a number of screening and definitive analytical techniques are presented in this section. First the chemical criteria for establishing the presence of oil in environmental samples of sediments and tissues are examined in detail through a suite of oil/tar samples and then

TABLE 2-17

GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYTICAL OUTPUTS

POLYNUCLEAR AROMATIC HYDROCARBONS
C_4 to C_6 Benzenes
Naphthalene
2-Methyl naphthalene
1-Methyl naphthalene
C_2 to C_4 Alkyl naphthalenes
Biphenyl
Acenaphthene
Fluorene
C_1 to C_3 Fluorenes
Phenanthrene
C_1 to C_4 Phenanthrenes
Dibenzothiophene
C_1 to C_3 Dibenzothiophene
Fluoranthene
Pyrene
C_1 Pyrene
Benzo(a)anthracene
Chrysene
C_1 Chrysene
Benzofluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
Perylene

these criteria applied to the sediments and tissues. Although stable isotope results are incorporated to some extent in this section, the isotopic results are presented in greater detail in Section 3.

2.3.1 Oils and Tars

The source evaluation strategy for oils/tars focused on three primary analyses: (1) FSCGC of saturated hydrocarbons to derive n-alkane information, (2) GC/MS of aromatic hydrocarbons, and (3) stable isotope ($\delta^{13}C$, δD, $\delta^{34}S$) measurements of hydrocarbon and asphaltene fractions. The first two are discussed in this section, with a summary of all techniques. Details of the stable isotope analyses will be found in Section 3.

2.3.1.1 UV/F Analyses

In order to establish the UV/F pattern of a variety of weathered oil residues from both the Ixtoc and Burmah Agate spills, a variety of oil/tar samples were analyzed by UV/F. The range of the resultant spectra indicates that Ixtoc and Burmah Agate oils exhibit similar fluorescence patterns, the latter having a greater abundance of compounds that fluoresce in the 310-nm (two-ring) region. However, the overall spectral appearance of the two oils is the same. In highly weathered Ixtoc residues (e.g., sample 8012-T05-1001, a 1980 beach tar, Figure 2-10), the spectrum takes on a markedly different appearance with the two-ringed aromatics severely depleted relative to the 1979 oils. Thus a range of UV/F spectral types are possible in environmental samples.

2.3.1.2 Alkanes by FSCGC

A set of 40 samples of waterborne oil, beached oil/tar, and oil associated with organisms was selected for analyses based on several criteria: (1) the samples should cover the geographical range of both spill impact areas, (2) the samples should represent oil available to the ecosystem both in 1979 and 1980 (mid- and post-spill), and (3) the samples should represent both offshore oil and beached oil.

FSCGC analysis first focused on the n-alkane distribution in the samples. N-alkane distributions in samples exhibited various degrees of weathering. As oil weathers, the n-alkanes are subject to loss from the samples. In this spill the losses were mainly through evaporation, as losses due to biodegradation were negligible (Boehm and Fiest, 1980a; Atlas et al., 1980). Thus when FSCGC traces such as Figure 2-11a are transformed to n-alkane relative abundance (NARA) plots, the weathering of the oil can clearly be seen. For example, an Ixtoc weathering sequence (Figure 2-12); Boehm et al., 1981) dramatically shows progressive loss of n-alkanes less than n-C_{23}.

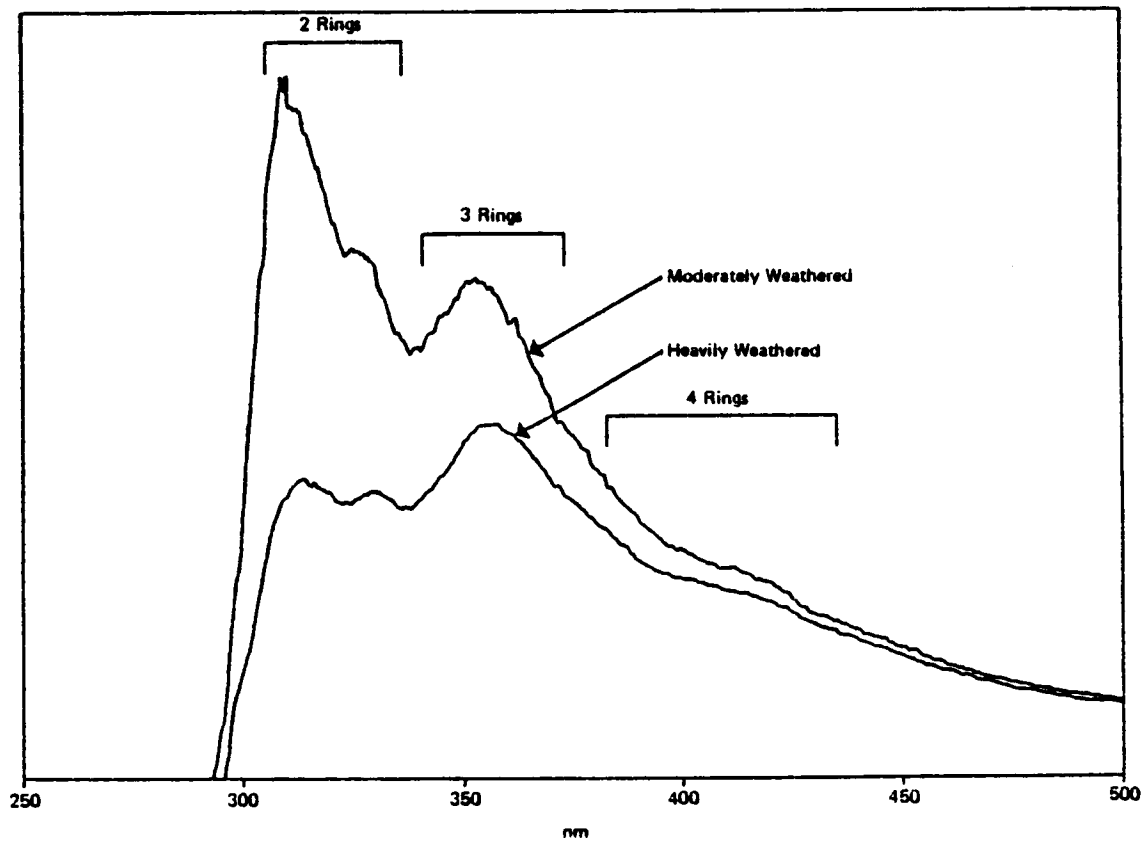


Figure 2–10. UV/F Synchronous Spectra of IXTOC Oils.

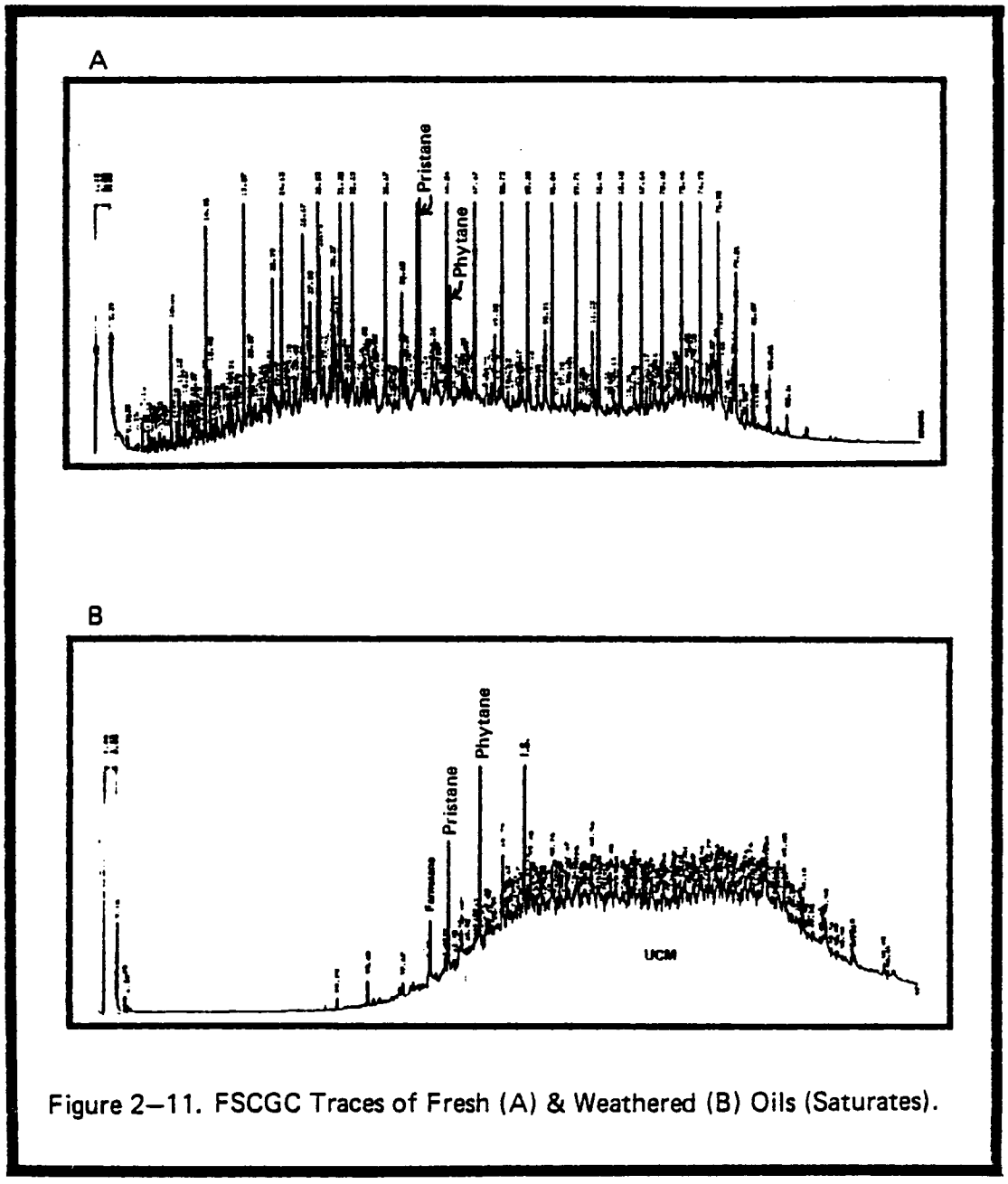


Figure 2–11. FSCGC Traces of Fresh (A) & Weathered (B) Oils (Saturates).

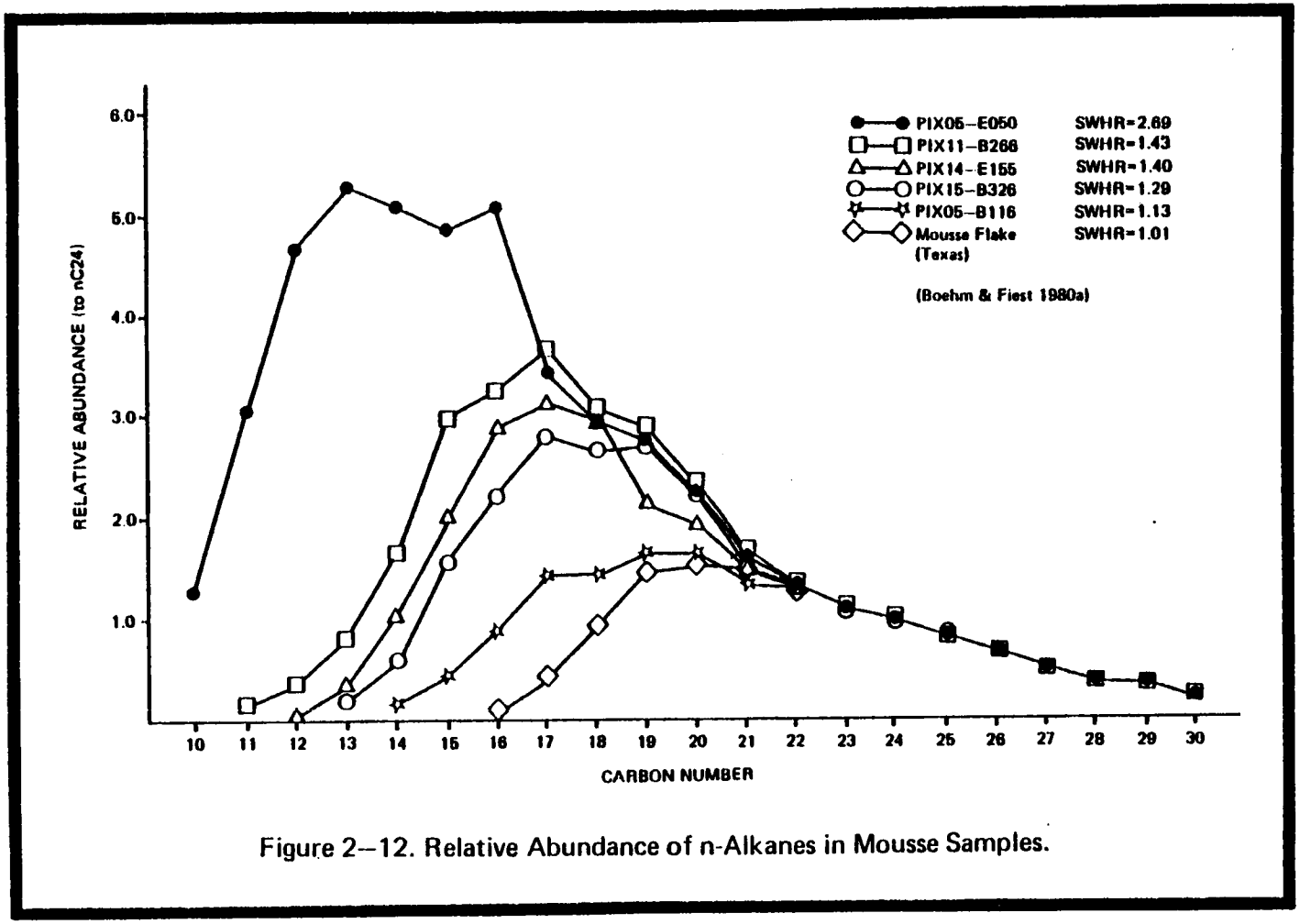


Figure 2--12. Relative Abundance of n-Alkanes in Mousse Samples.

In order to "bracket" the possible Ixtoc compositions on the NARA plots, three samples were selected as representative of three possible weathered Ixtoc residues. The three samples chosen were obtained during the Researcher/Pierce cruise (Boehm and Fiest, 1980a) to the wellhead and during the Longhorn IV cruise off the Texas coast in August 1979 as large patches of Ixtoc mousse (water-in-oil emulsion) entered Texas waters (Patton et al., 1981). These samples then served as reference oils to the 1979 oil/tar collections. Any oil/tar alkane compositions falling into the compositional window illustrated in Figure 2-13 were judged to be Ixtoc-probable oils.

A series of oil samples whose compositions fall within this window are shown in Figure 2-14. In contrast, two other compositions were observed. The first consists of fresh and weathered Burmah Agate oils (Figure 2-15) and the second of two paraffinic beach tars associated with neither spilled oil (Figure 2-16).

Although all of the 1979 oil/tar samples exhibited n-alkane components, thus allowing the evaluation presented above, the 1980 beach tar collection consisted of highly weathered, n-alkane depleted petroleum residues (e.g., Figure 2-11b). These isoprenoid-dominant FSCGC traces, the product of microbial weathering, precluded n-alkane source evaluation. In these cases other source evaluation techniques were required (GC/MS of aromatics; stable isotopes analysis).

2.3.1.3 Aromatic Hydrocarbons in Oils/Tars by GC/MS

For this study the aromatic hydrocarbon composition of petroleum has been classified into two groups: (1) two- and three-ring aromatics and their alkyl homologues, and dibenzothiophene (a sulfur heterocycle) and its alkyl homologues, and (2) four- and five-ring aromatics. The first group of aromatic compounds is dominant in fossil fuel aromatic compositions, especially the alkyl homologues of naphthalene, fluorene, phenanthrene, and dibenzothiophene, and therefore these compounds can be termed petrogenic aromatics. The second group consists of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzofluoranthene, benzopyrenes, perylene, and their methyl homologues. These compounds, if present in petroleum, are usually present at lower concentration levels than the first group. These polynuclear aromatic hydrocarbon (PAH) compounds are ubiquitous in the geosphere, but their presence in the environment is usually attributable to pyrogenic sources (combustion of fossil fuels; Laflamme and Hites, 1978) rather than to petroleum itself.

Phenanthrene and anthracene, both three-ringed parent (unsubstituted) compounds, are found in both groups. However, alkylated members of these homologous series are more abundant than the parent compounds in petroleum, while the parent compound is more abundant in pyrogenic PAH assemblages. Thus, the abundances of alkylated phenanthrenes/anthracenes relative to the parent compounds are keys to the determination of the presence of petroleum. As petroleum weathers, the alkylated dibenzothiophenes and alkylated phenanthrenes become prominent residuals and become key diagnostic parameters for identifying oils (Boehm et al., 1981; Overton et al., 1981).

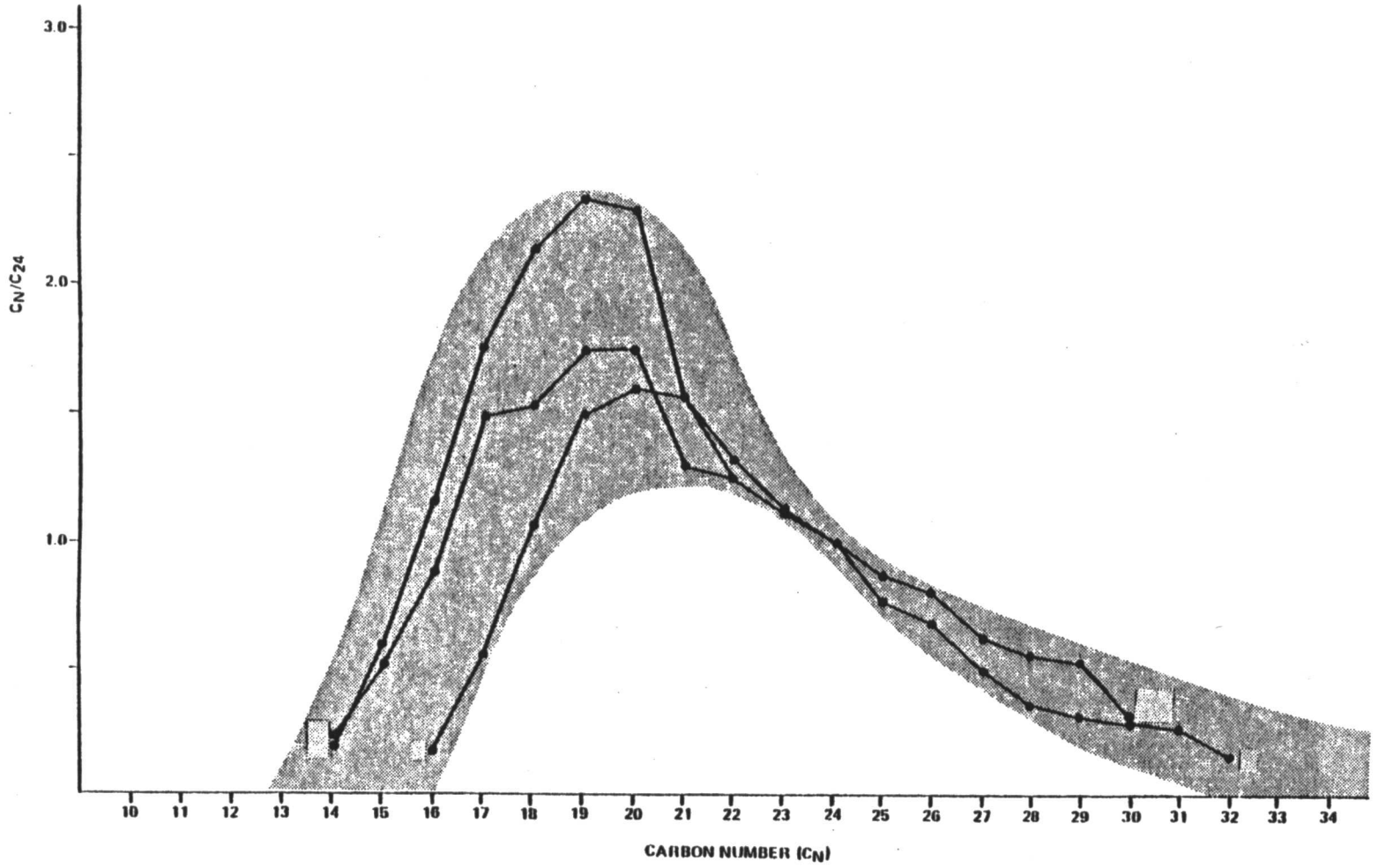


Figure 2–13. NAPA Plots Showing Range of Compositions of Weathered Ixtoc I Reference Oils.

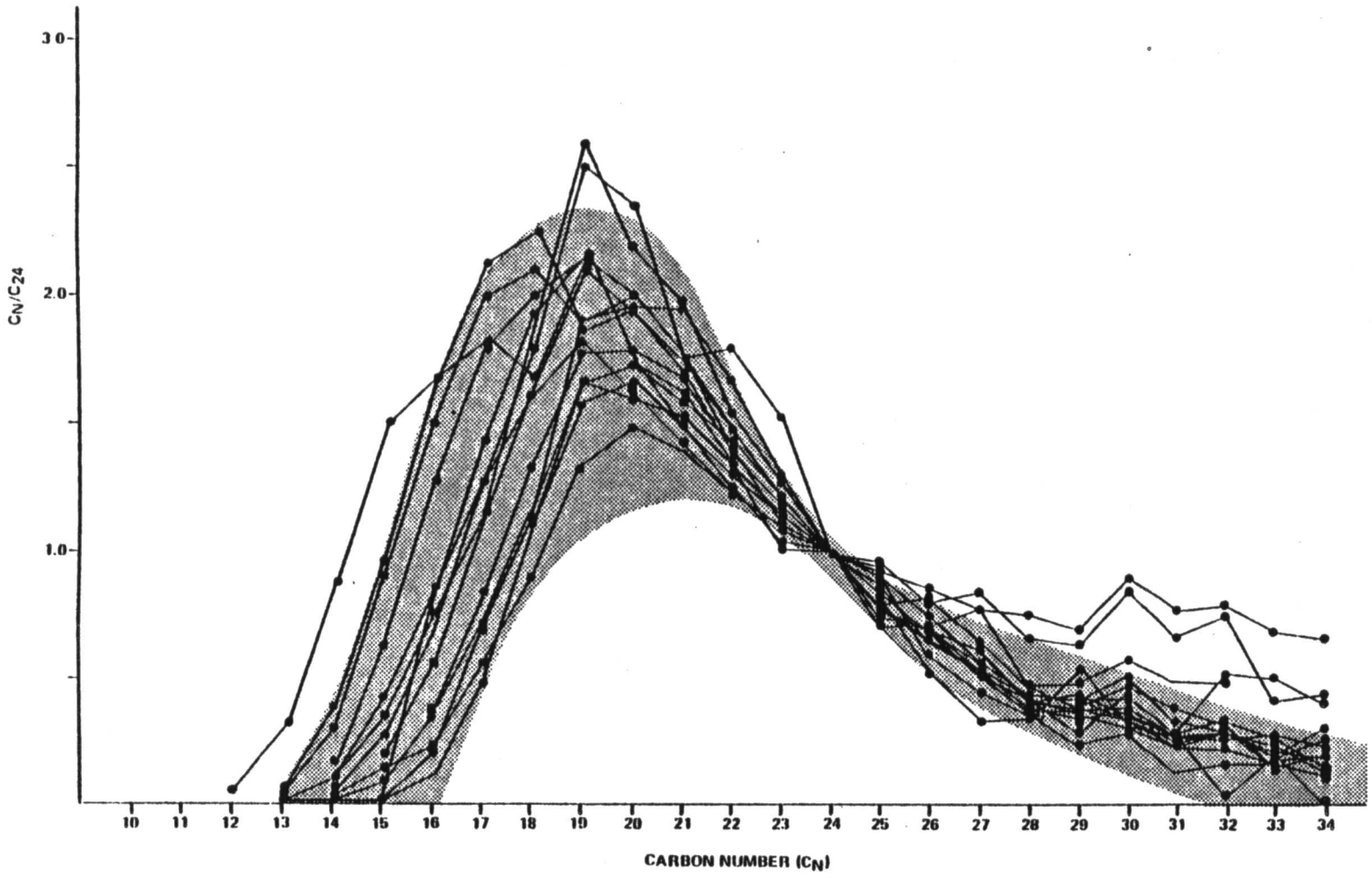


Figure 2—14. Composite NARA Plots of Ixtoc I - Related Oils/Tar.

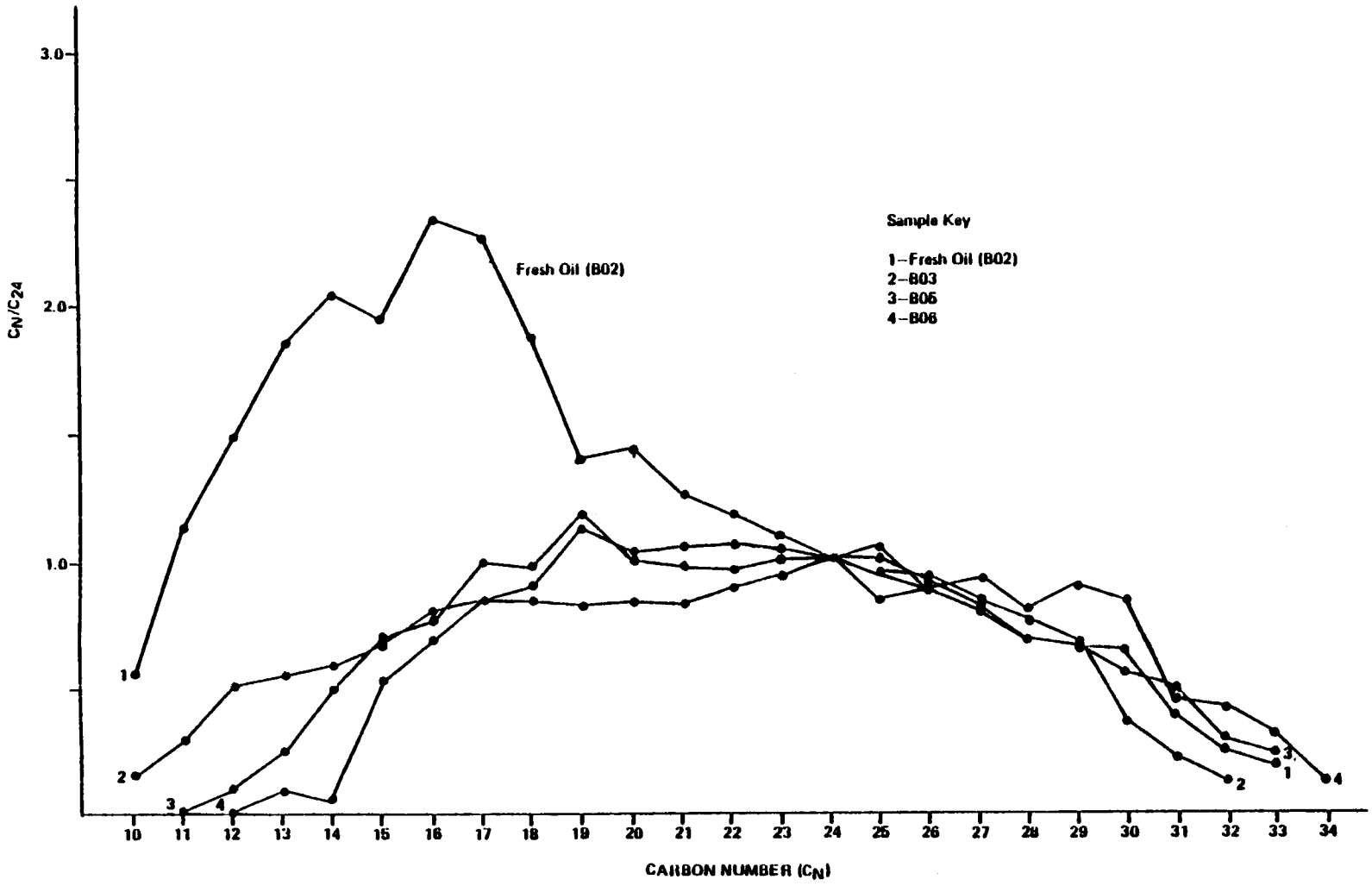


Figure 2–15. NARA Carbon Plots of Burmah Agate Related Oils in Various States of Weathering.

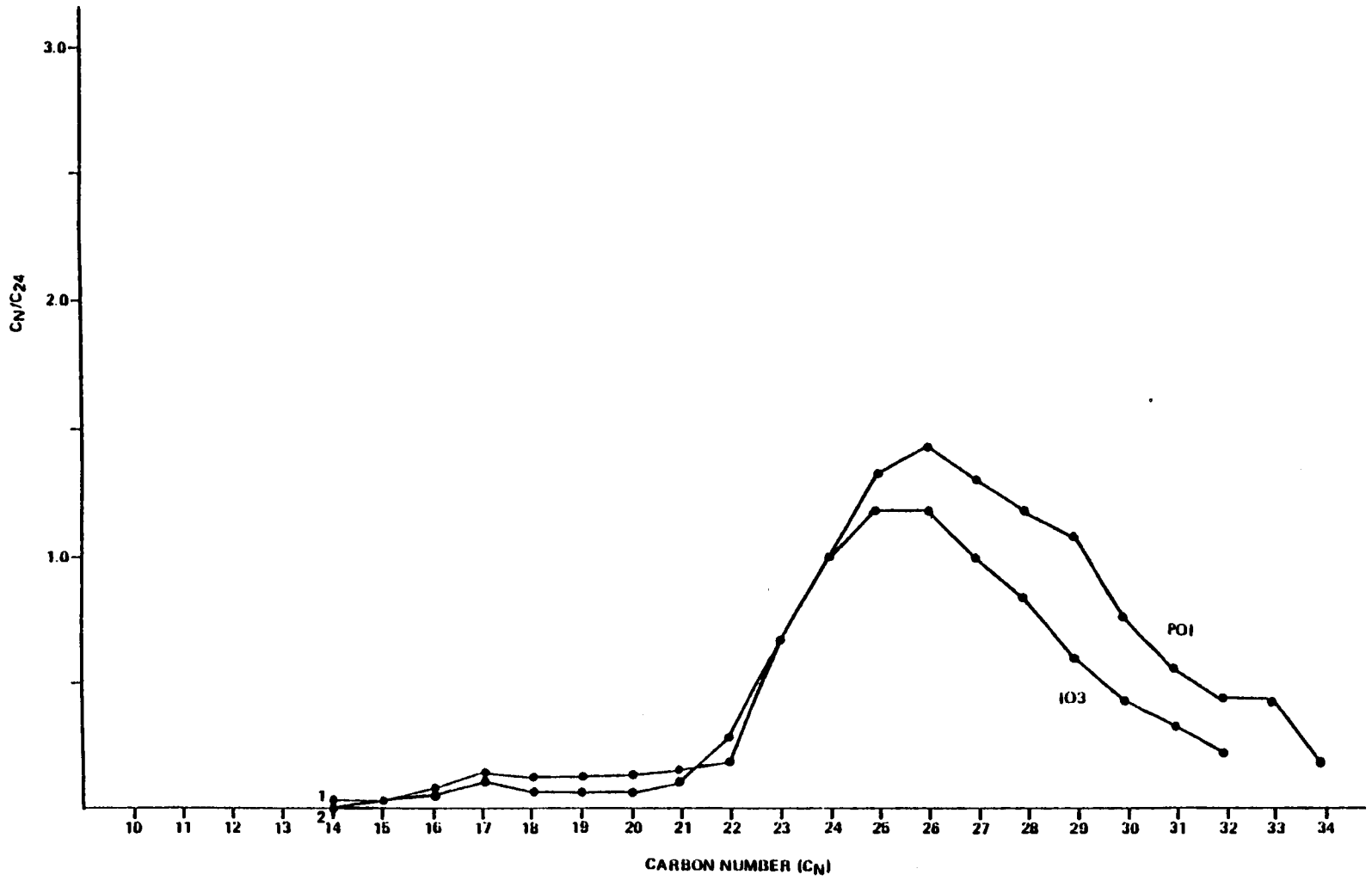


Figure 2—16. NARA Plots of Non-Spill Related Beach Tars.

The purpose of examining the aromatic content of environmental petroleum samples in the Texas Gulf Coast region is to decipher the origin of the oil. Petroleum samples analyzed as part of this phase of the program include Ixtoc I oil from the wellhead, weathered Ixtoc I oil near wellhead, floating oil collected at a distance from the wellhead (Hooper Collection), beached oil and tar (1979 and 1980), and Burmah Agate oil. The resultant quantitative aromatic data are presented in Appendix 9.1. The remainder of the investigation focuses on the Group I aromatic composition of the petroleum samples, because of their importance in identifying petroleum, and in establishing the presence of oil in environmental samples (Sections 2.2.3.3 and 2.2.5.2). Quantitative data on Group I aromatics in fresh and weathered Ixtoc and Burmah Agate oils are presented graphically in Figure 2-17 where the much greater relative abundance of these compounds in Burmah Agate oil is evident.

The recent presence of oil in the Texas Gulf Coast region is not necessarily indicative of an Ixtoc source. Other petroleum sources prevalent in the region (e.g., platform drilling discharges, tanker accidents and discharges) have produced small spillages, tar balls, etc. (Jeffrey et al., 1973; Geyer, 1981) and may confuse the evaluation of the impact of Ixtoc I to this environment. The Burmah Agate accident is of particular concern because the incident occurred near the area of the Ixtoc I oil contamination and oil spread to the Ixtoc impact region. The composition of Group I aromatics may be quite different for various petroleums. However, weathering may drastically alter the relative aromatic content of petroleum exposed to the environment, preferentially depleting lower molecular weight aromatics (e.g., Boehm et al., 1981a; Atlas et al., 1981). This is shown in Figure 2-17, where the relative petrogenic aromatic content of representative oil samples is depicted for selected fresh and weathered oils.

Overton et al. (1981) have suggested that a passive chemical tag may be useful in distinguishing different oils. Their suggestion involves comparing ratios of C_1, C_2, and C_3 alkyl phenanthrenes (m/e = 192, 206, 220) to the respective C_1, C_2, and C_3 alkyl dibenzothiophenes (m/e = 198, 212, 226). The relative quantities of each compound from a selected oil sample are shown in the GC/MS extracted-ion current profiles shown in Figures 2-18 and 2-19. A compilation of these ratios for the oil samples examined by GC/MS is presented in Table 2-18.

The alkyl phenanthrene-alkyl dibenzothiophene ratios for the fresh wellhead Ixtoc I oil and the Ixtoc I oil floating in the vicinity of the wellhead are nearly identical. The C_2 and C_3 ratios for the beached Ixtoc oils and ing effects. This is most pronounced for the C_1 ratios of the beached and floating petroleum. The elevation of C_1 ratios is probably the first indication by this method that weathering processes are affecting the phenanthrene (P) and dibenzothiophene (DBT) aromatic compositions. Two of the three floating oil samples (7908-Q01-1001, 7908-Q03-1001) again show good C_2 and C_3 ratio correlations to the Ixtoc I oil, but C_1 ratios were also slightly elevated. Burmah Agate oil was also examined and found to be quite different from Ixtoc I oil Burmah Agate C_1 ratios were about five times greater than Ixtoc I, C_2 ratios about six times larger, and C_3 ratios about four times larger.

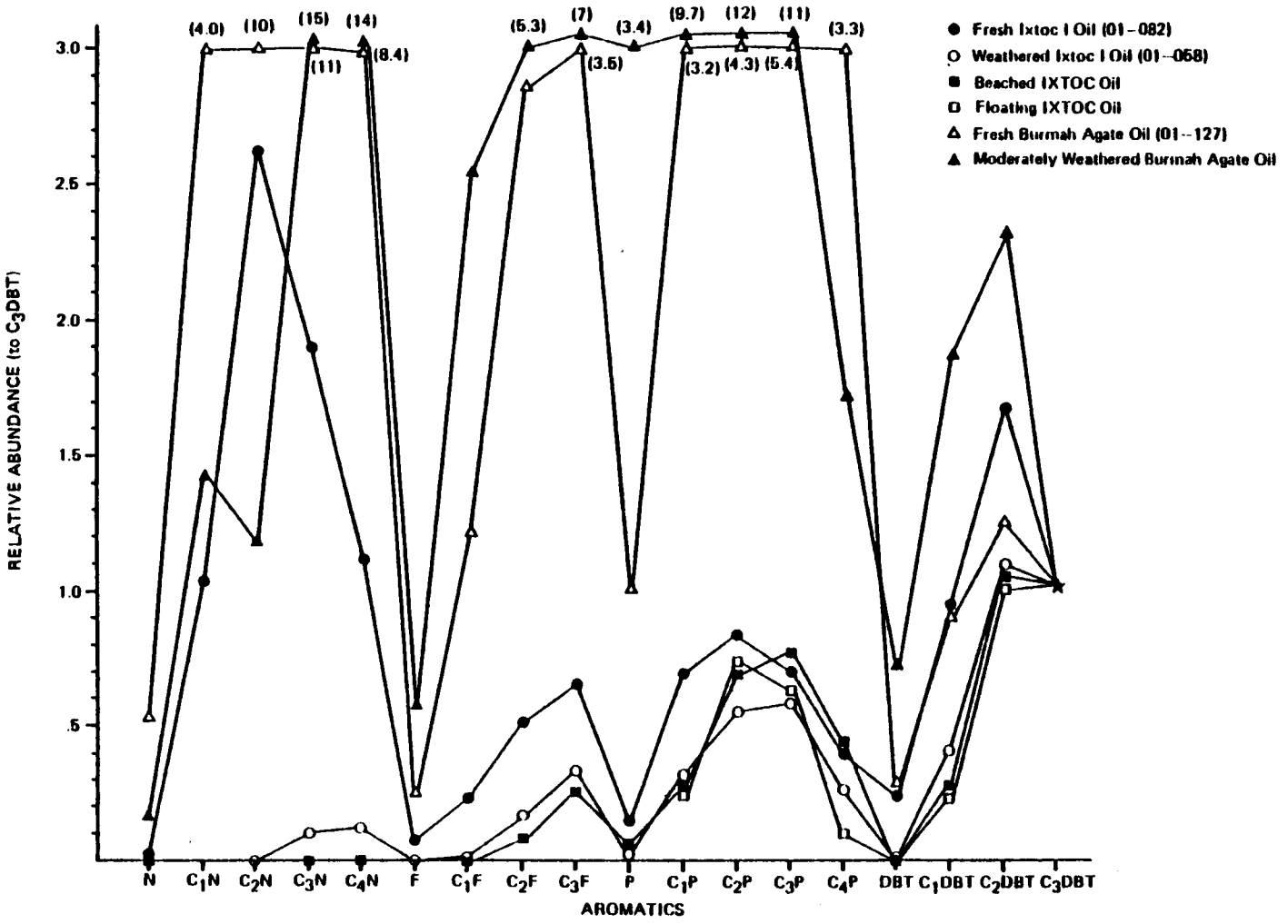


Figure 2–17. Group I Aromatics in Oils.

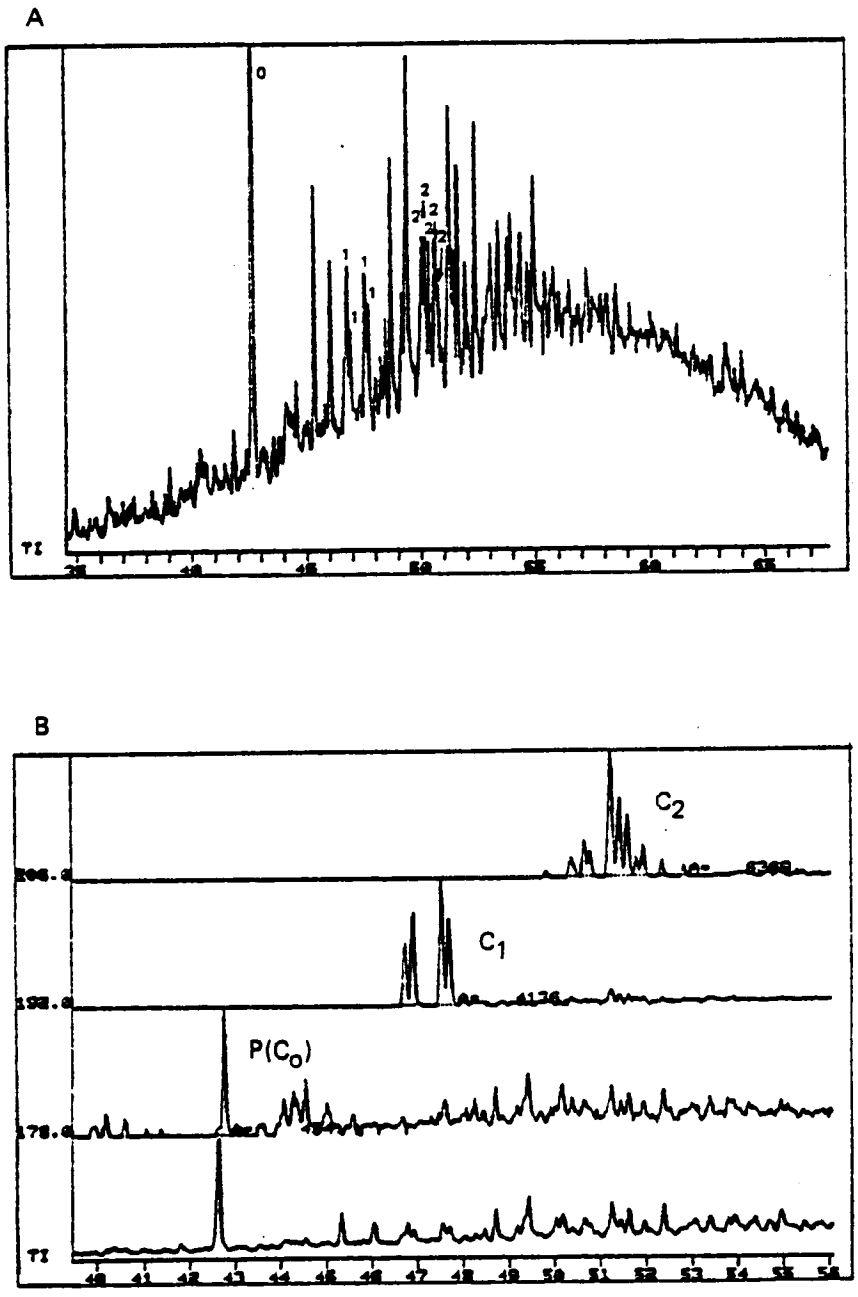


Figure 2–18. GC/MS Analysis of Oils, A = Total Ion Chromatogram, B = Phenanthrene Series Mass Chromatograms.

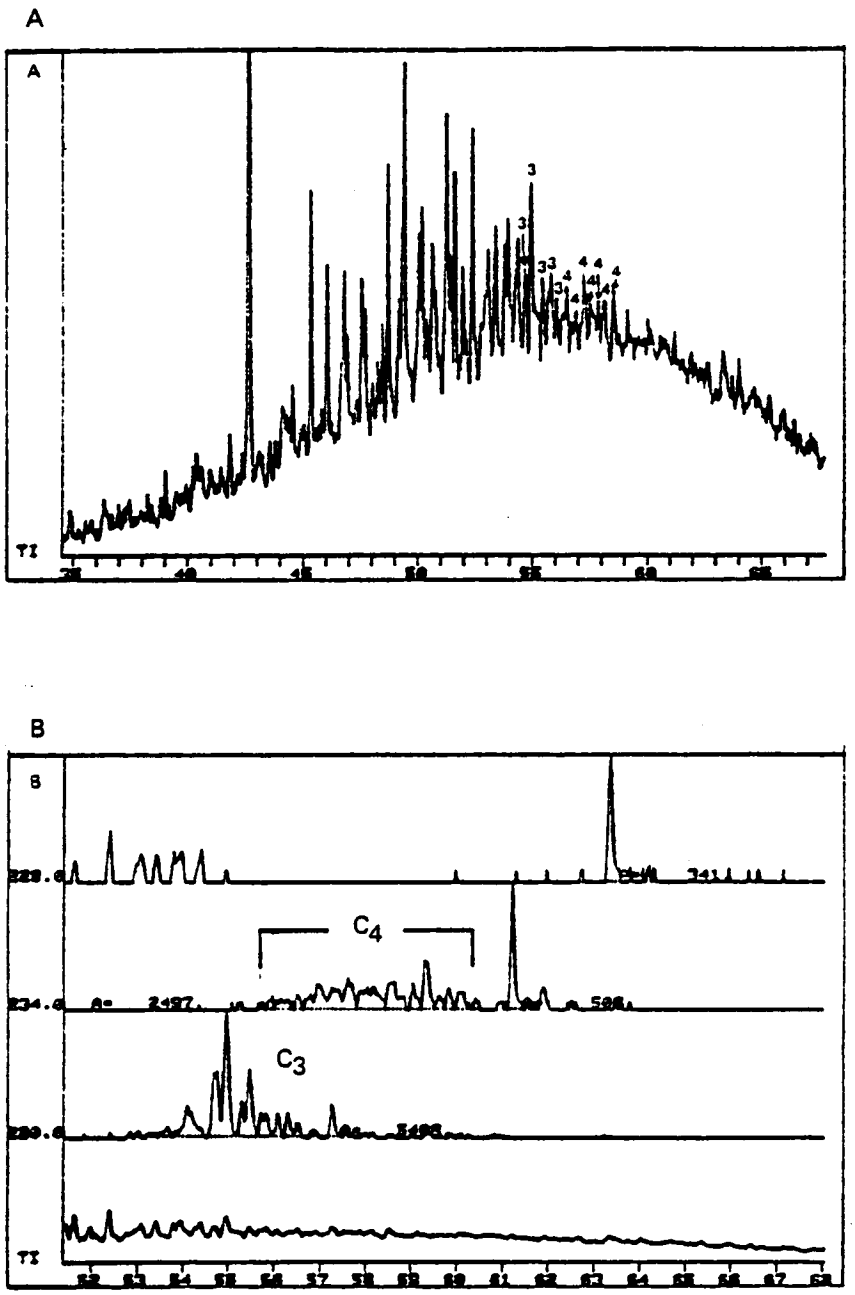


Figure 2—18. (Continued).GC/MS Analysis of Oils, A = Total Ion Chromatogram, B = Phenanthrene Series Mass Chromatograms.

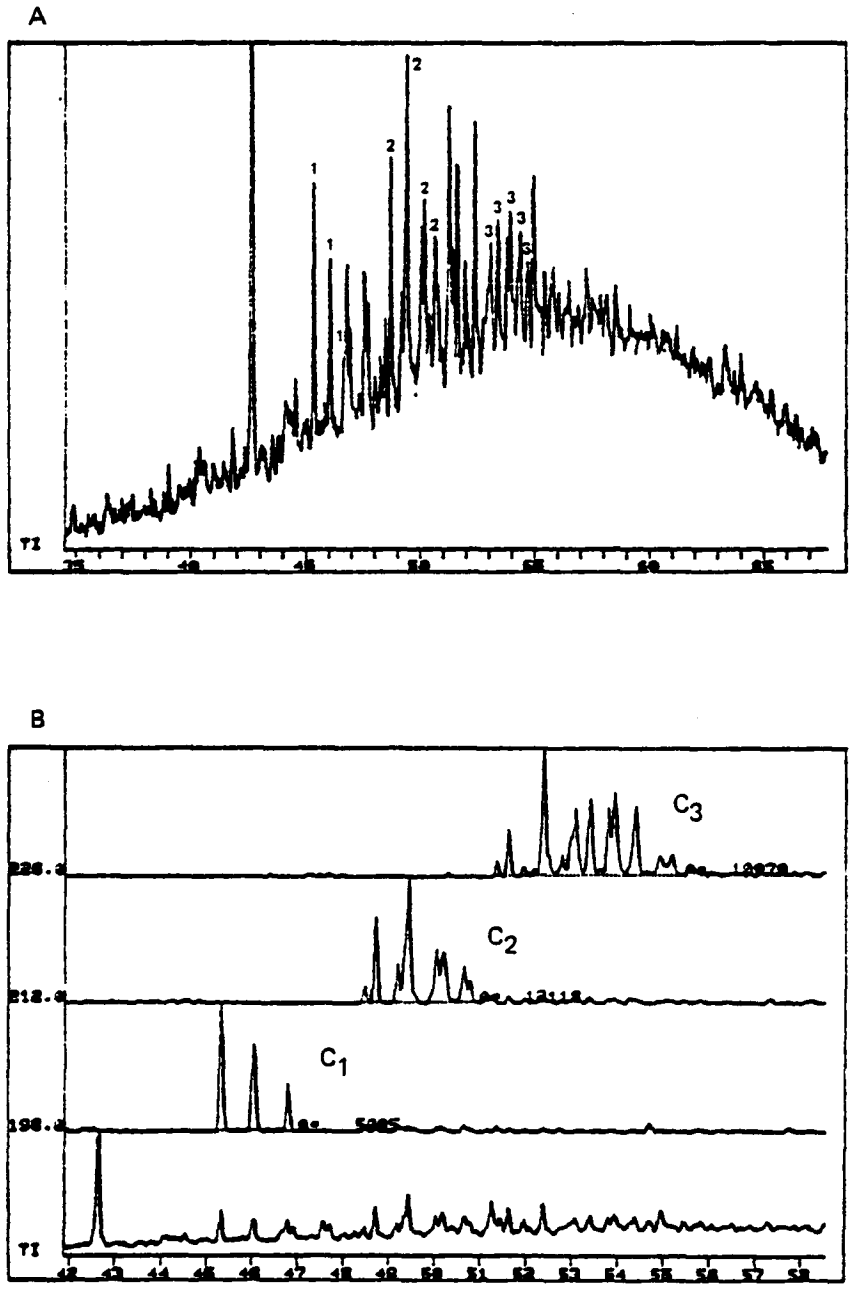


Figure 2–19. GC/MS Analysis of Oils, A=Total Ion Chromatogram, B=Dibenzothiophene Series Mass Chromatogram.

TABLE 2-18

PETROLEUM ALKYL PHENANTHRENE-ALKYL DIBENZOTHIOPHENE RATIOS

SAMPLE	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT
Ixtoc Collection			
Fresh Oil From Wellhead			
PIX-5-E050[a]	0.72	0.51	0.69
Weathered Ixtoc I Oil Near Wellhead			
Texas mousse flake[b]	0.89	0.43	0.59
Texas mousse[b]	0.73	0.41	0.49
PIX-5-B116[a]	0.82	0.48	0.69
PIX-17-E186[a]	0.89	0.48	0.58
Beached Ixtoc Oils and Tars[c]			
7908-I4C-1001	1.02	0.66	0.78
7911-P20-1001	1.18	0.64	0.76
7911-P06-1001	1.32	0.60	0.80
Overall Ixtoc (Range)			
	0.72-1.32	0.41-0.66	0.49-0.80
Burmah Agate Collection			
Floating Oil			
7911-B02-1001	3.56	3.41	5.36
7911-B02-1002	5.69	4.80	11.36
Beached Oil			
7911-B03-1001	5.06	5.11	11.02
Overall Burmah Agate (Range)			
	3.56-5.69	3.41-5.11	5.36-11.36

TABLE 2-18 (CONT.)

SAMPLE	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT
Identified Oils/Tars[d]			
Beached Oil/Tar (Ixtoc)			
7912-P12-1001	1.03	0.57	0.71
8004-E02-1001	0.65	0.47	0.66
8004-E05-1001	0.90	0.67	0.72
8012-T01-1001	1.41	0.49	0.68
8012-T02-1001	1.18	0.53	0.70
8012-T03-1001	1.65	0.56	0.60
8012-T05-1001	0.86	0.57	0.62
Beached Oil/Tar (Burmah Agate)			
7911-B04-7001	4.92	4.52	9.47
7911-B04-1002	5.68	3.67	6.15
Floating Oil (Ixtoc)			
7908-Q03-1001	1.06	0.62	0.63
7908-Q01-1001	2.20	0.62	0.69
Unidentified Oils/Tars			
Beached Oil/Tar			
7911-P02-1001	2.15	1.40	1.52
Floating Oil/Tar			
7908-Q02-1001	6.17	4.20	5.44

[a]Data from Researcher cruise, September 1979 (Boehm and Fiest, 1980a).

[b]Data from Patton et al., 1981.

[c]Definitively identified by FSCGC and stable isotopes.

[d]Based on determined ranges of C_2 and C_3 ratios.

Based on the range of the C_2 and C_3 ratios, identifications of oil/tar samples are made in Table 2-19. Two samples definitely are not of either origin (P02 and Q02). Note that even the very highly weathered beached oil/tar collection (i.e., 8012-T series) is identifiable through the C_2 and C_3 ratios.

By incorporating the results of the alkyl phenanthrene-alkyl dibenzothiophene ratios with saturated hydrocarbon FSCGC data and carbon, hydrogen, and sulfur stable isotope data, the source of many of the oils can be determined (see Table 2-19). At least two matches are needed to assign a sample to a category. Results from stable isotope analyses are weighted more strongly than FSCGC results alone. Sulfur stable isotope data are tentatively used to overturn FSCGC results but C and H isotope data are overruled by a combination of FSCGC and GC/MS data (e.g., sample 8012-T03-1001).

When the GC/MS results are combined with FSCGC and isotope results, the overall results are definitive. The power of the aromatic ratios in confirming oil identifications, and in establishing identities if one of the other techniques is questionable, is evident (Table 2-19).

2.3.1.4 Aromatic Sulfur Compounds by Hall Detector

Analysis of oils by sulfur-specific GC detectors has previously been used in conjunction with GC-FID to fingerprint oils (ASTM 3328-78; USCG, 1977). However, no attempt at such an evaluation on heavily weathered oils has been documented.

Ten oil samples representing a range of Ixtoc and Burmah Agate samples were analyzed by this method. The FSCGC-Hall trace (e.g., Figure 2-20) offers much information on at least two homologous organo-sulfur compound series, the dibenzothiophenes (DBT) and naphtho-dibenzothiophenes (NDBT). In several samples a dibenzothiophene compound series is discerned but, as these compounds are relatively rapidly weathered from waterborne oils, source-matching using this compound series is limited to use in conjunction with a normalizing parameter (e.g., the alkylated phenanthrenes; Section 2.3.1.3).

Both the Ixtoc and Burmah Agate oils contain similar series of DBT and NDBT compounds. When graphed together to examine the compositional details of the DBT series (Figure 2-21), a wide range of compositions is observed. The methyl DBT (peaks C, D, and E) appears to fall into two groupings. Although the Burmah Agate oils appear relatively "rich" in methyl DBT, so does one Ixtoc residue. The other Ixtoc oils cluster fairly close to one another in the C, D and E compounds, but so do several residues not believed to be Ixtoc-related due to isotopic evidence. Much more scatter in the data appears in the relative compositional plots for the dimethyl dibenzothiophenes (peaks F-I).

Some heavily weathered samples do maintain their organic-sulfur profiles, in spite of a radical weathering of the n-alkane components. This was previously apparent in GC/MS studies.

TABLE 2-19

SUMMARY OF RESULTS OF OIL IDENTIFICATION PROCEDURES[a]

COLLECTION	ERCO ID	FSCGC RESULTS[b]	ISOTOPE RESULTS (C,H,S)[b]	GC/MS RESULTS[b]	OVERALL[b]
HOOPER	7908-Q01-1001	I	0	I	I
	7908-Q02-1001	0	0	0	0
	7908-Q03-1001	I	0	I	0?
	7908-Q04-1001	I	I	-	I
	7908-Q05-1001	W	0	-	0
ERNST	8004-E02-1001	I	I	I	I
	8004-E03-1001	0	I	-	I
	8004-E04-1001	I	I	-	I
	8004-E05-1001	W	I	I	I
	8004-E01-1001	I	I	-	I
STURTEVANT	7911-P02-1001	0	B	0	0
	7911-P17-1001	I	-	-	ID
	7911-P20-1001	I	I	I	I
	7911-P24-1001	I	I	-	I
	7911-P06-1001	I	I	I	I
	7911-P09-1001	I	I	-	I
	7912-P12-1001	I	I	I	I
RPI	7908-I4C-1001	I	I	I	I
	7908-I5A-1001	I	I	-	I
	7911-B11-1001	W	-	-	ID
	7909-I03-1001	0	-	-	ID
USCG	7911-B04-1001	B	B	B	B
	7911-B02-1001	B	B	B	B
	7911-B02-1002	B	B	B	B
	7911-B06-1001	B	B	-	B
	7911-B04-1002	B	B	B	B

TABLE 2-19 (CONT.)

COLLECTION	ERCO ID	FSCGC RESULTS[b]	ISOTOPE RESULTS (C,H,S)[b]	GC/MS RESULTS[b]	OVERALL[b]
BURMAH AGATE	7911-P01-1001	O	-	-	ID
	7911-B05-1001	B	B	-	B
	7911-P19-1001	O	-	-	ID
	7911-B07-1001	B	B	-	B
	7911-B03-1001	B	B	B	B
1980 BEACH SURVEY	8012-T01-1001	W	I	I	I
	8012-T02-1001	I	O	I	I
	8012-T03-1001	W	O	O	O
	8012-T04-1001	W	I	-	ID
	8012-T05-1001	W	I	I	I
	8012-T06-1001	W	-	-	ID
TURTLES	7908-CM2-1001	I	-	-	ID
	7908-CM1-1001	O	-	-	ID
USCG-COIL SAMPLE	155	I	-	-	I

[a]Refer to Appendix 9.1 for cross referencing and location of all samples.

[b]I - Ixtoc.
B - Burmah Agate.
O - Other source or questionable match.
W - Weathered Beyond Recognition.
ID - Insufficient data.

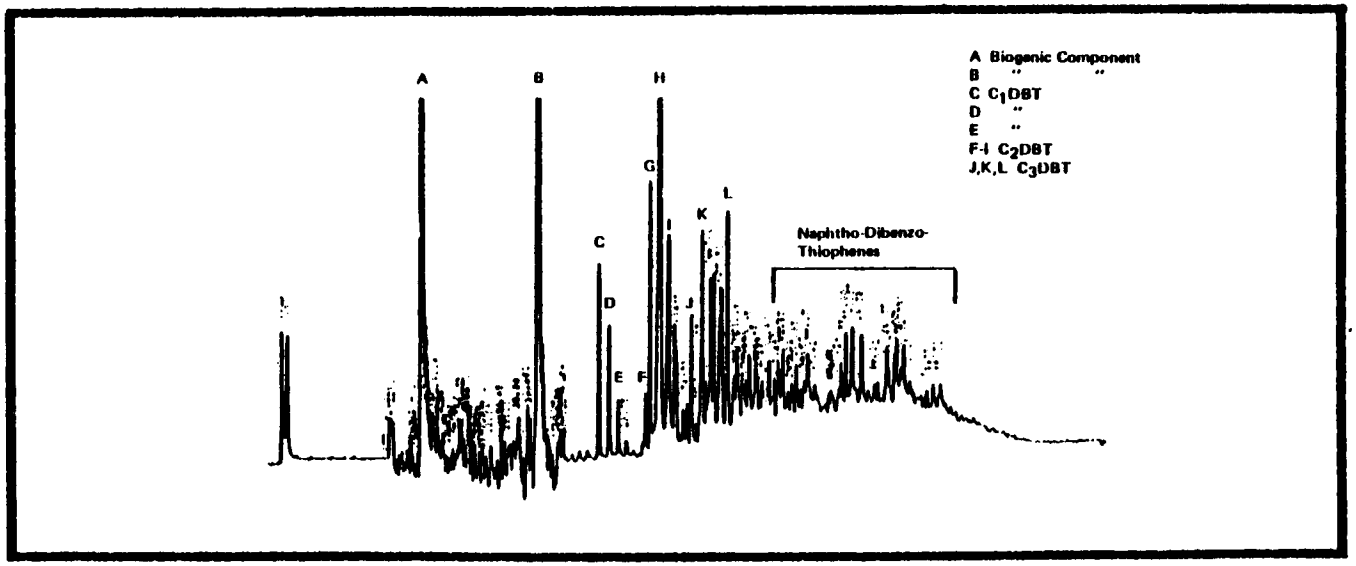


Figure 2–20. Capillary Hall Detector (S Mode) Trace of Beached IXTOC Oil (Letters Refer to Figure 2–21).

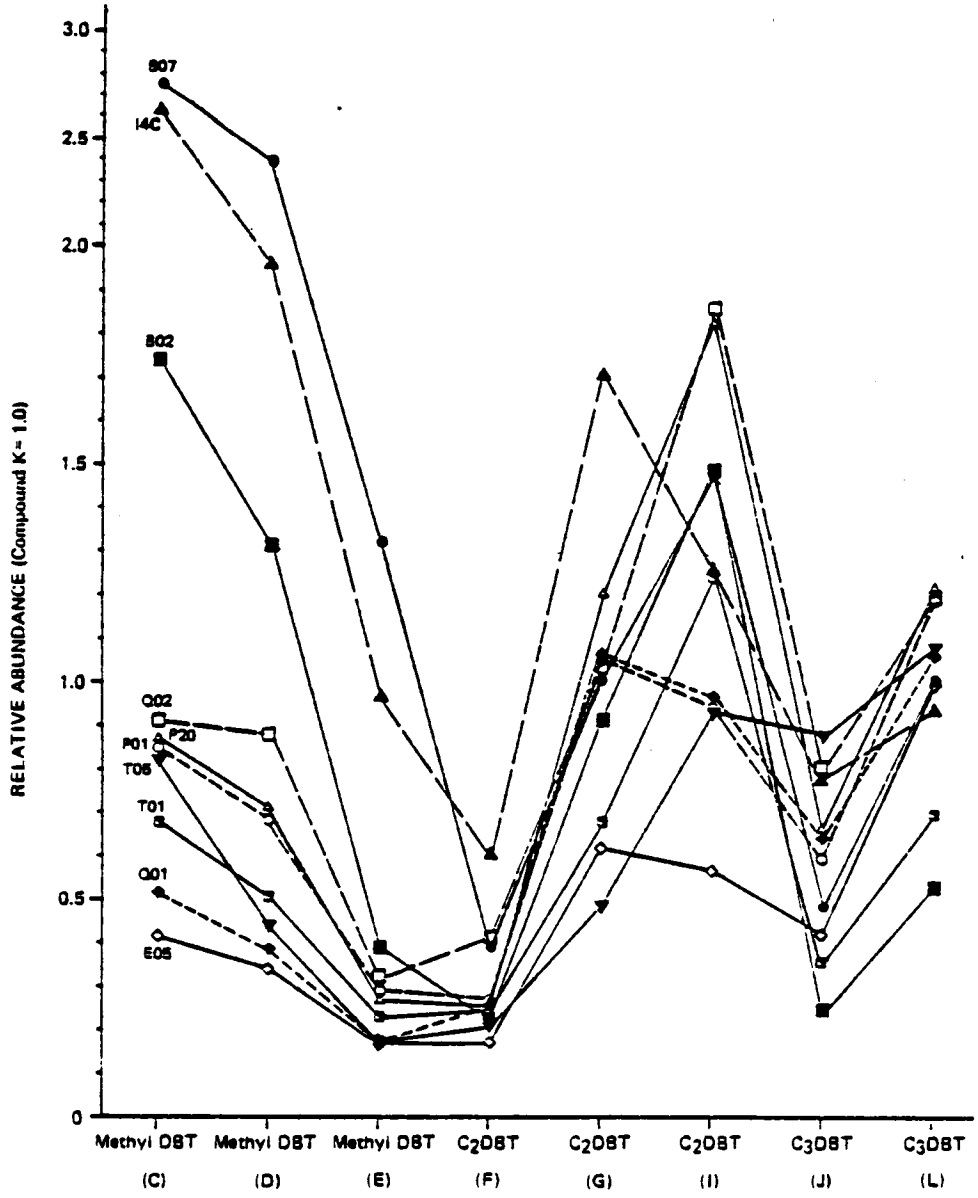


Figure 2–21. Compositional Plots of FSCGC–Hall (S Mode) Derived Information.

2.3.1.5 Azaarene Compounds

Ten oil samples were subjected to the acidic extraction, neutralization, solvent back-extraction scheme to isolate the basic organo-nitrogen heterocyclics. Most of the samples contained only small traces of these compounds made up mainly of the highly alkylated three-ringed acridine/phenanthridine series. GC/MS was used to examine these distributions (Figure 2-22). The predominant azaarenes in weathered Ixtoc and Burmah Agate oils show that these compounds (m/e 207, 211, 233) are more abundant in the Ixtoc oil than in the Burmah Agate oil but that little information of a source-matching nature can reliably be gained by azaarene evaluations due to the extremely low levels of these compounds.

2.3.2 Petroleum Hydrocarbons in the Benthic Substrate

One hundred and twenty-five samples were screened for the presence of petroleum residues by UV/F, and eighty-three were further subjected to detailed FSCGC (FID) analysis to quantify both the saturate (f_1) and aromatic (f_2) fractions. Of the 83 samples analyzed by FSCGC, 40 were analyzed by GC/MS to determine detailed aromatic hydrocarbon and sulfur heterocyclic compositions.

2.3.2.1 UV/F Screening

A serial addition of whole Ixtoc oil was added to a low-level sediment sample extract, to determine the ease of recognition of newly deposited oil residues in offshore sediments by UV/F. The data presented in Figure 2-23 indicate that Ixtoc oil can be seen at levels as low as 0.25 mg oil per ∿100 grams of original sample (2.5 $ng \cdot g^{-1}$). However, there is a substantial amount of background fluorescence in many Gulf Coast samples (Boehm and Fiest, 1980c; Figure 2-24) similar in the overall UV/F spectrum to the oil. Therefore false positive or indeterminate UV/F screenings are quite probable occurrences, indicating that further, more detailed, discriminating analytical work is necessary to differentiate the background from small incremental oil additions.

Roughly half of the sediment samples screened were considered to be "petroleum-possible" samples. UV/F traces such as those shown in Figure 2-25 were commonly encountered. Samples were selected for further analysis based on the similarity of UV/F spectra to the spectra of weathered Ixtoc oil. Samples were also selected for overriding geographical considerations. UV/F results might not have indicated obvious oil, but sufficient historical data existed (i.e., the 12 primary STOCS stations) and thus pre- to post-spill comparisons could be made.

All sediment samples exhibited UV/F spectral maxima in the two, three and four aromatic compound bands (e.g. Figure 2-25). The perylene doublet (five rings) was a prominent feature of many of the offshore samples. In a

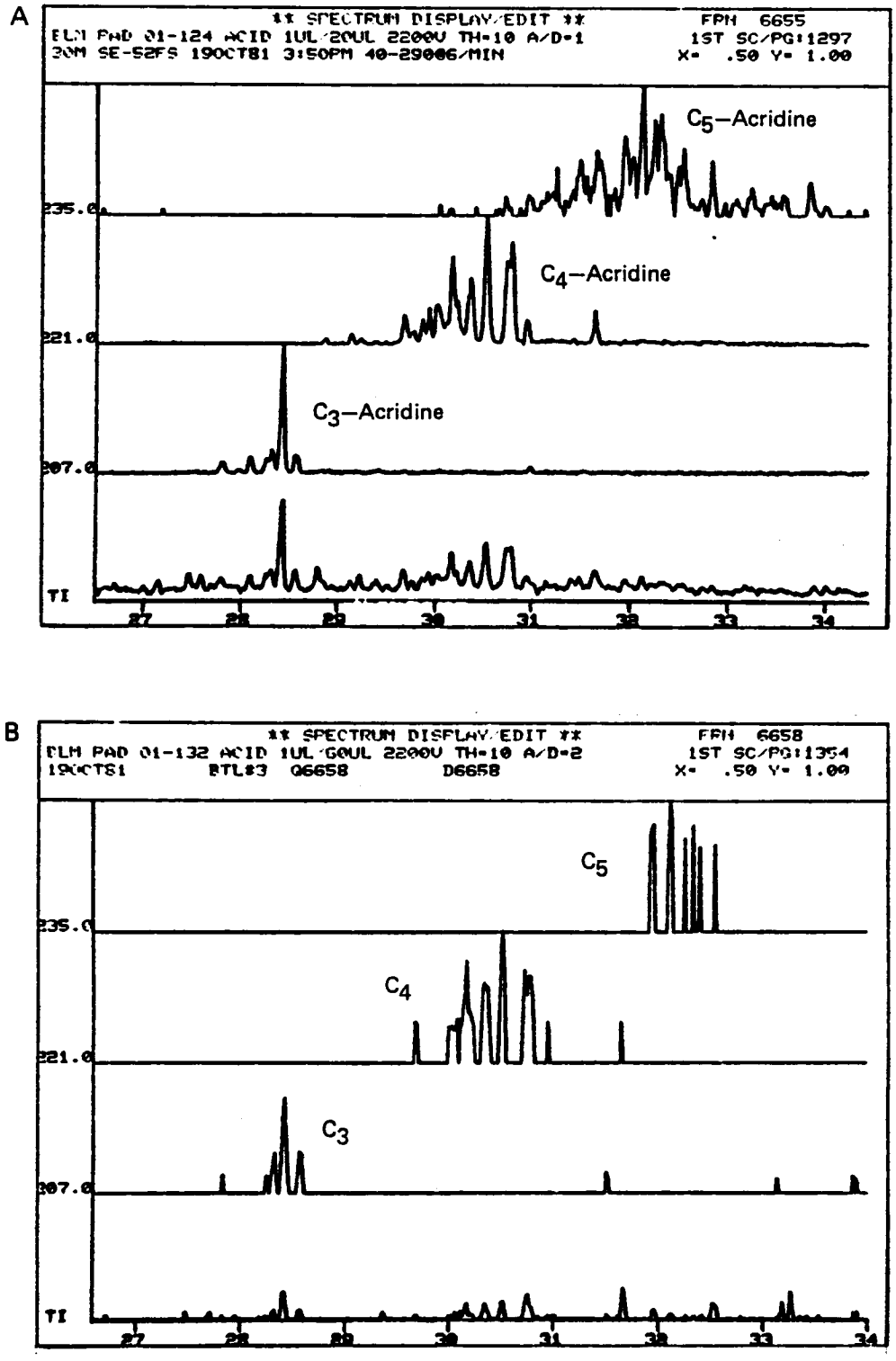


Figure 2–22. GC/MS Mass Chromatograms of Alkylated Acridine/Phenanthridine Compounds in Weathered Ixtoc I Oil (A) and Weathered Burmah Agate Oil (B).

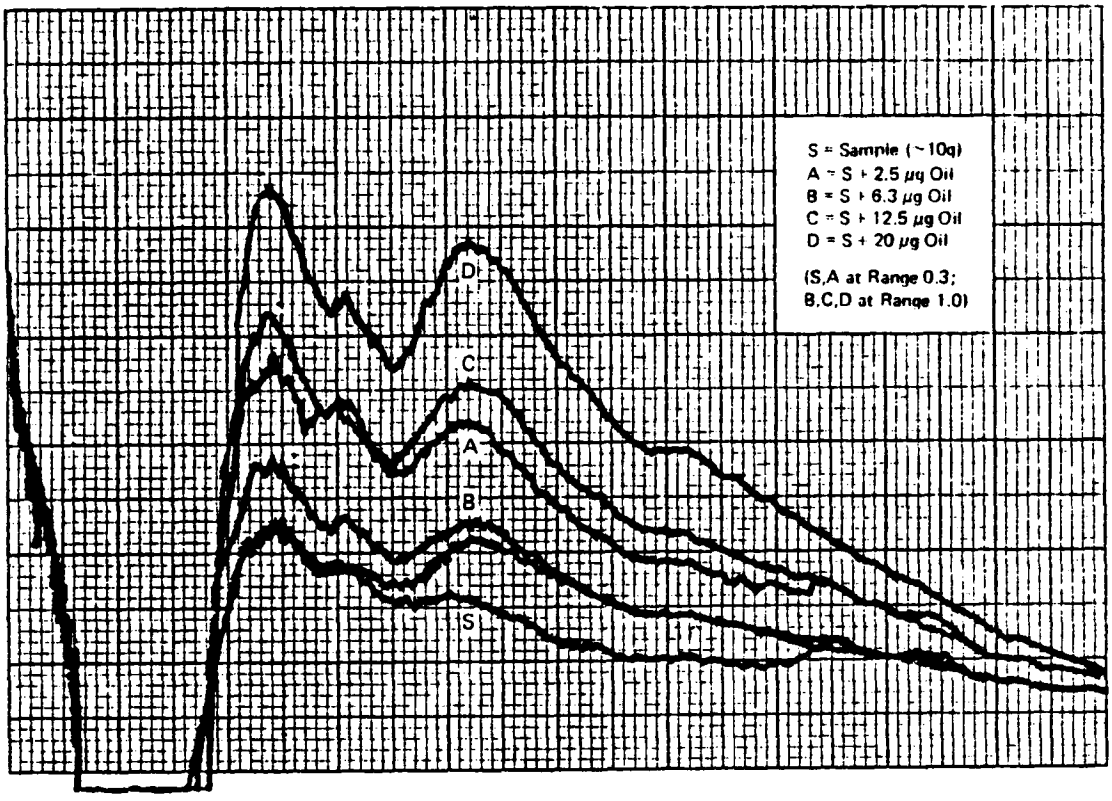


Figure 2–23. UV/F of Serial Addition of Ixtoc I Oil to Sediment.

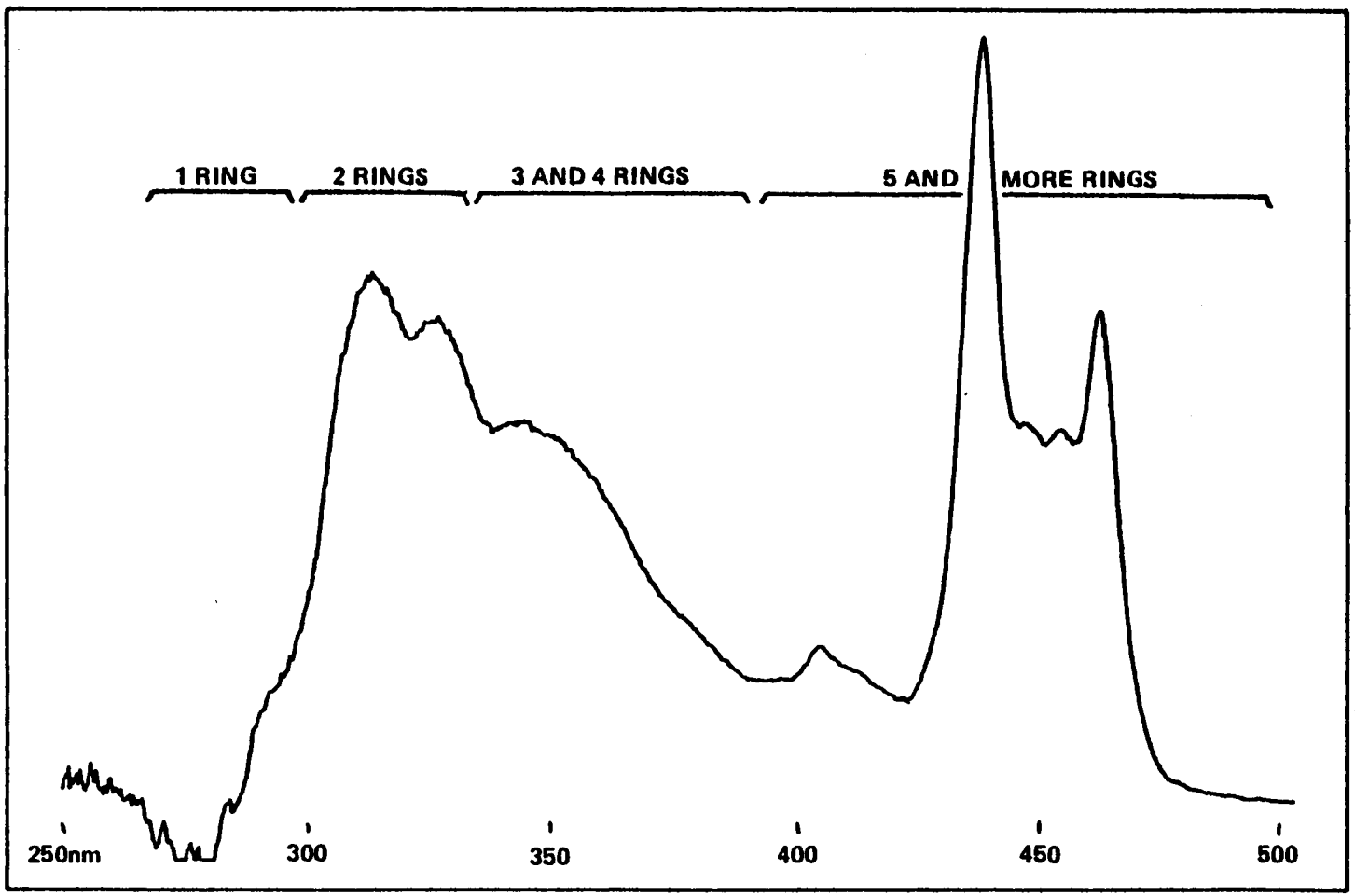


Figure 2–24. Synchronous Spectrofluorometry Spectrum of Gulf of Mexico Sediment Extract Showing the Resolution of Ring Classes and Perylene in the Right-Hand Side of the Spectrum.

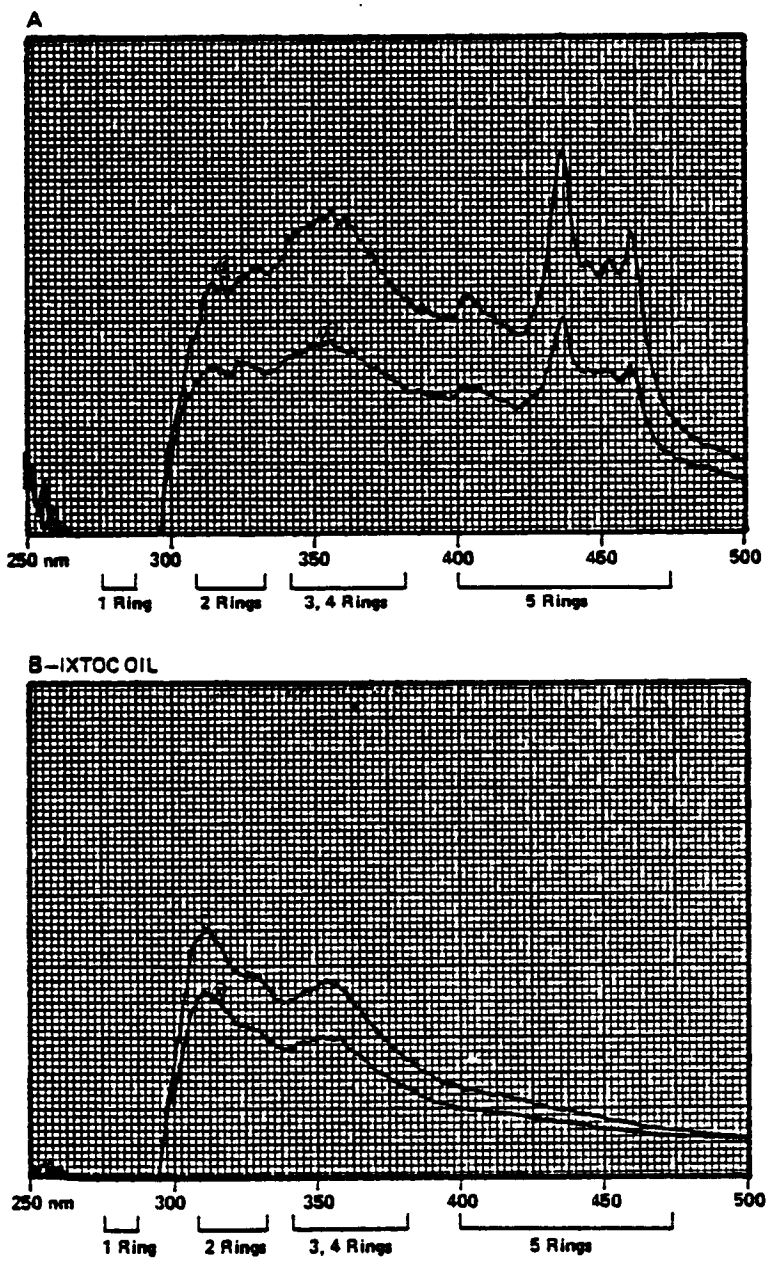


Figure 2–25. Sychronous UV/F Spectra of Sediment Sample Showing Typical Gulf of Mexico Background (A) Mixed with Possible Oil Contamination.

sample such as that shown in Figure 2-25a small incremental additions of oil would be difficult to discern from the fluorescent background characteristic of many Gulf coast sediments (Boehm and Fiest, 1980c).

2.3.2.2 FSCGC Analysis

On those samples selected for further analysis, FSCGC was used to obtain quantitative results on the gross saturated and aromatic fractions, and to obtain quantitative information on individual components (n-alkanes, isoprenoid alkanes), component groupings, and component ratios. Those parameters quantified and stored in the data base are shown in Table 2-14. Most of these parameters were available in the 1975-1977 STOCS data and were calculated here in anticipation of data comparisons.

Summaries of the total hydrocarbon levels observed in the sediments as determined from FSCGC traces are presented in Figures 2-26 and 2-27.

Concentrations fell into the 0.5-20 ppm range throughout the study area. In general, the hydrocarbon concentrations determined were directly related to the total organic carbon (TOC) content of the sediment and, at least on the gross (ppm) level, had no connection with Ixtoc I or Burmah Agate petroleum additions. For the most part PHC levels in sediments seem to be dictated by the geochemical ratio of PHC/TOC $\sim$0.006 (or 0.6%) throughout the study region. PHC versus TOC plots have been previously employed as diagnostic tools for looking at hydrocarbon sources (Boehm and Fiest, 1980c; Boehm, 1978). In nearshore nonpolluted sedimentary environments subjected to background inputs of PHC (i.e., chronic inputs) the PHC/TOC ratio will remain relatively constant if similar sources dictate the hydrocarbon geochemistry of the sediment. If oil from a spill should impact a sampling site, a proportionately greater amount of PHC will be added to the sediment as the PHC/TOC ratio in oils is very large ($\geq$ 0.5). Thus small additions of oil, on the order of 10 ppm, should easily be detected via PHC/TOC plots such as those shown in Figures 2-28 and 2-29.

Several 1979 and 1980 samples appear to be atypical of the regions' geochemical makeup (i.e., fall off the regression) and thus should be evaluated further for the presence of oil. This was accomplished by evaluating FSCGC traces and derived parameters to differentiate new petroleum additions from the 0.5-20 ppm background. FSCGC traces were scrutinized for weathered but nonbiodegraded oil, as biodegraded oil was found in 1980 samples from the south Texas beaches (Figure 2-11b), and for indications of local inputs such as source material from the Port Aransas Channel area (Figure 2-30).

Sediment samples from the study area subjected to FSCGC analysis and scrutinized for any gas chromatographic indication of recent oil (e.g., Figures 2-31, and 2-32) failed to produce any trace of spill-derived oil. Indications of weathered oil inputs were noted in the Burmah Agate sediment collection and will be discussed below. In addition, low levels

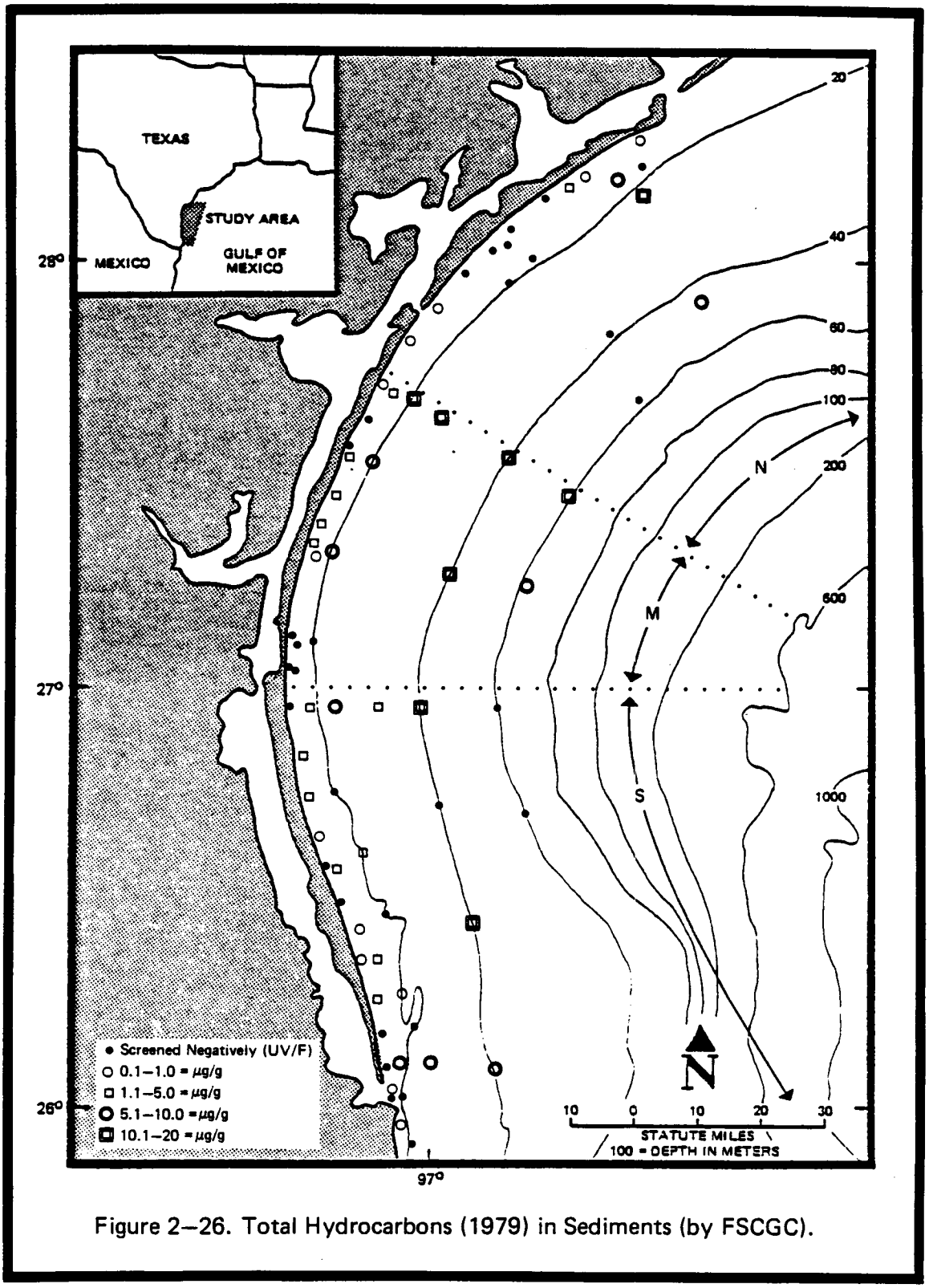


Figure 2–26. Total Hydrocarbons (1979) in Sediments (by FSCGC).

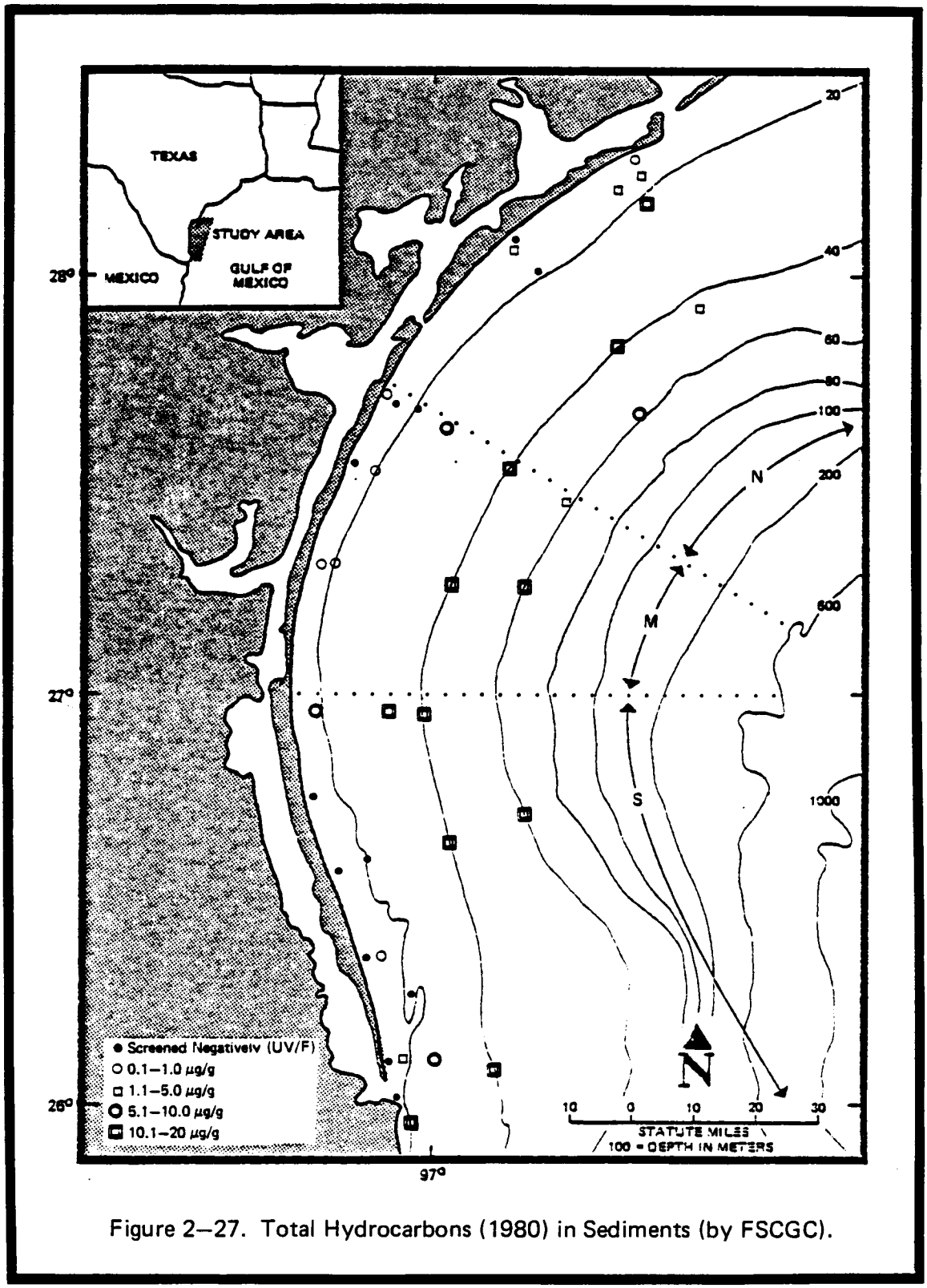


Figure 2–27. Total Hydrocarbons (1980) in Sediments (by FSCGC).

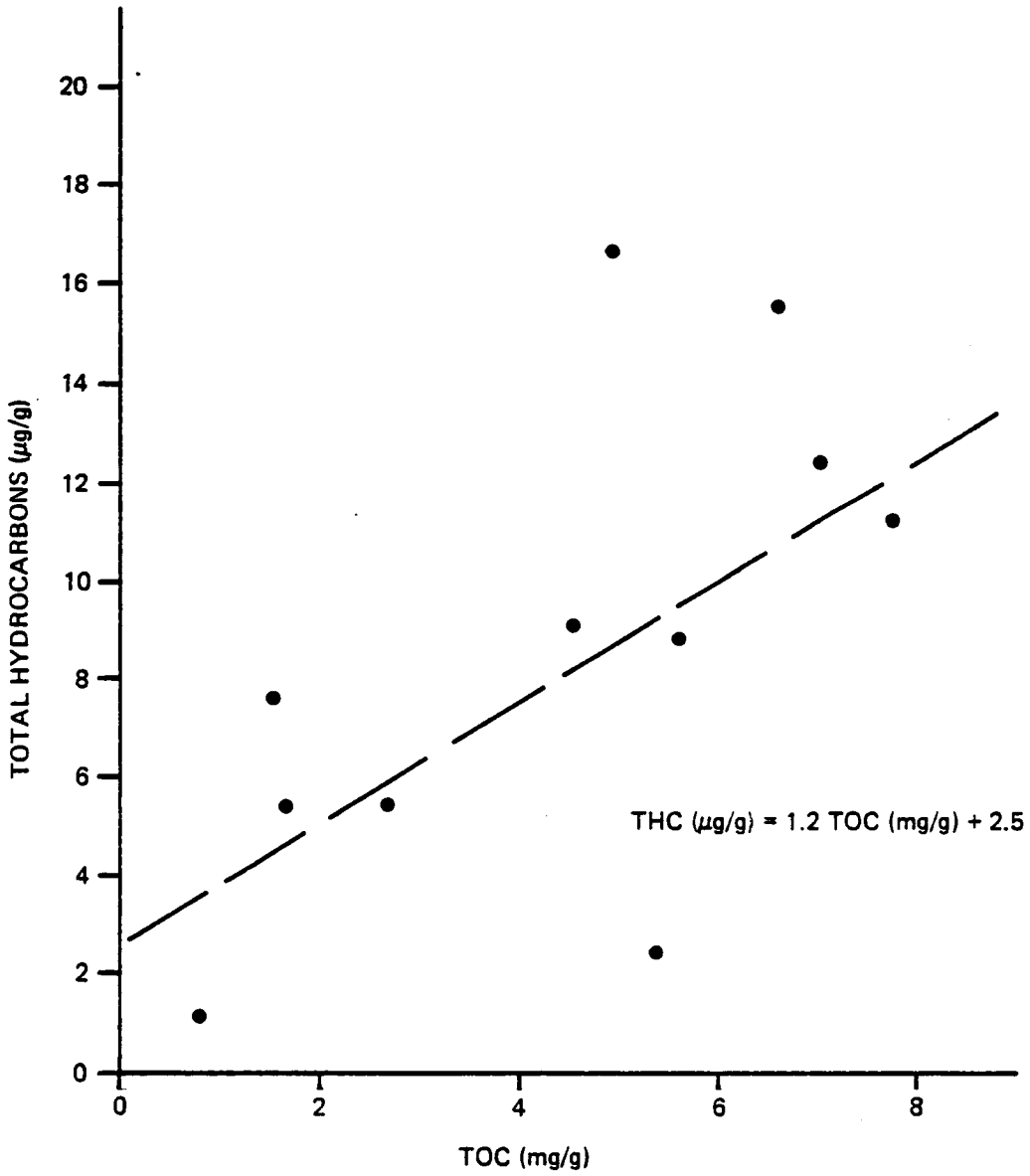


Figure 2–28. Total Hydrocarbon Concentrations in Sediments as a Function of TOC (1979).

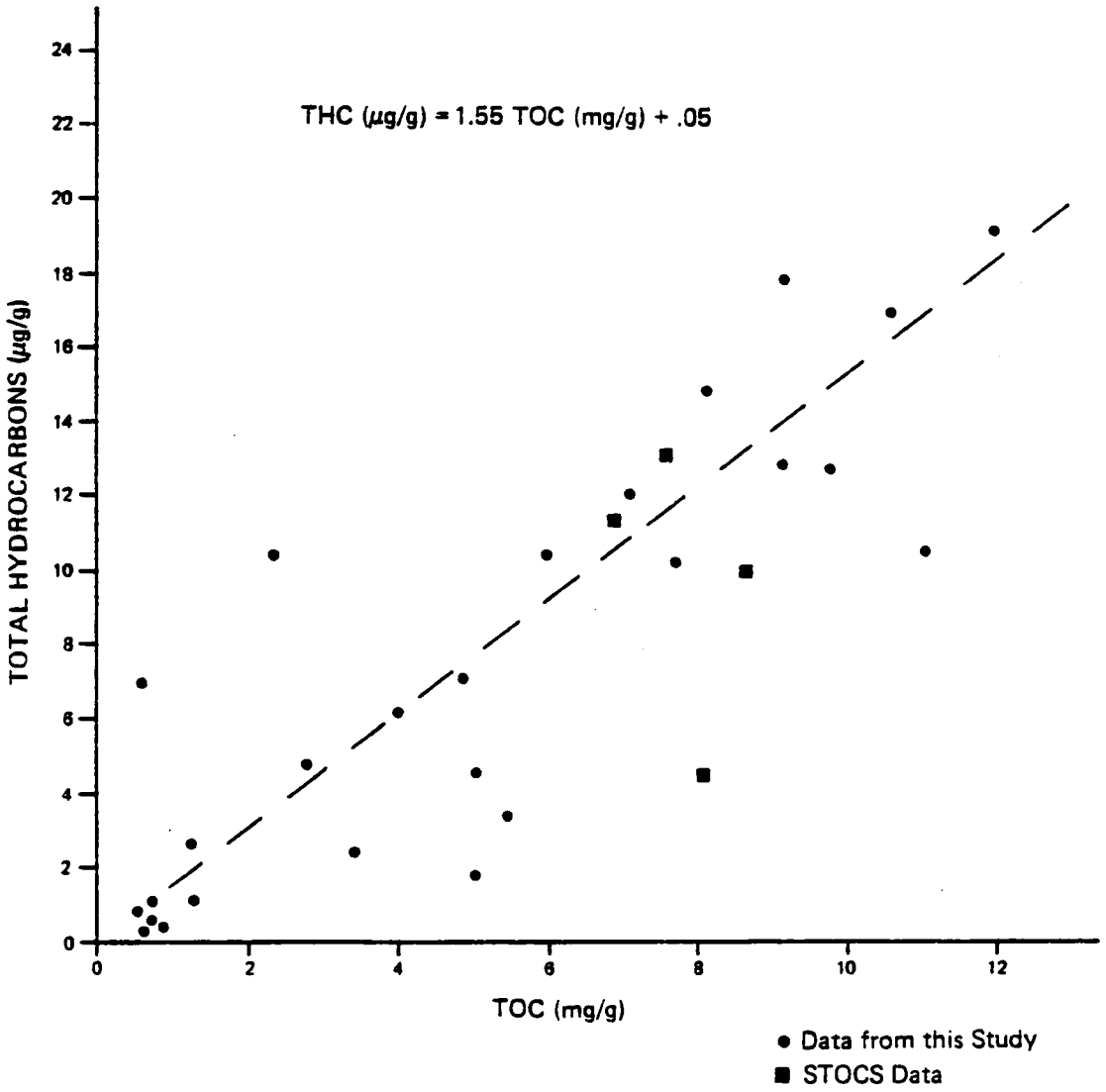
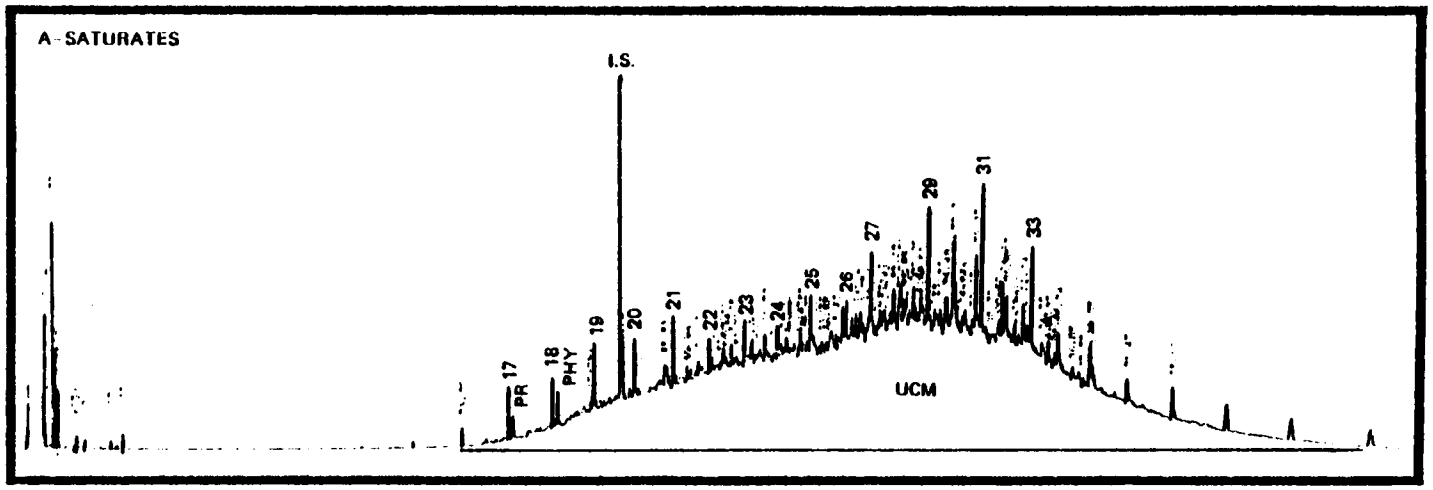


Figure 2–29. Total Hydrocarbon Concentrations in Sediments as a Function of TOC (1980).



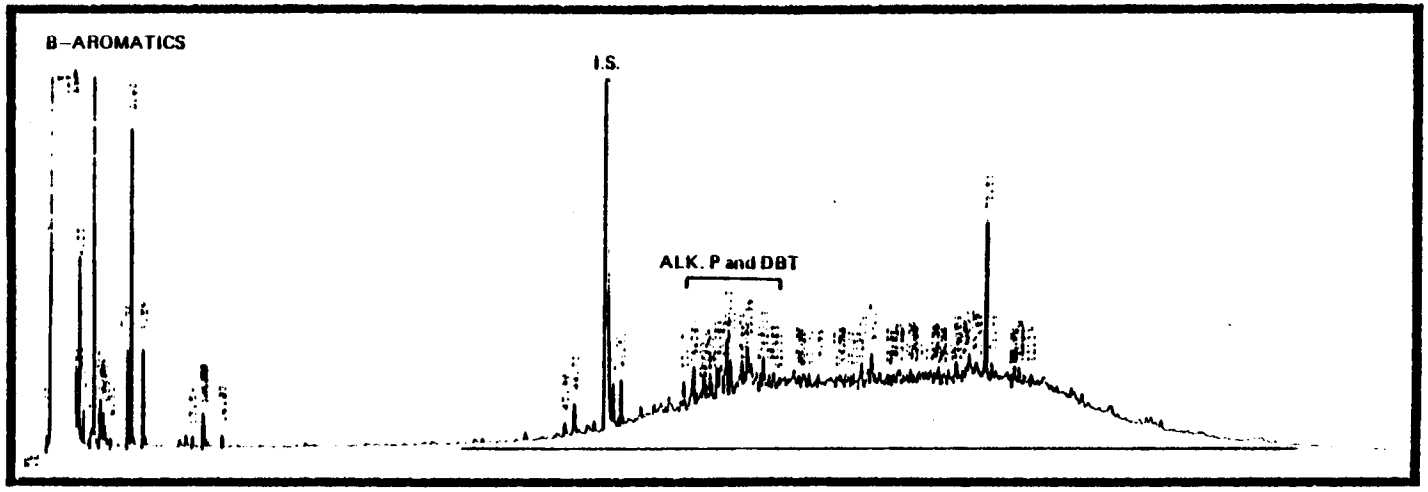
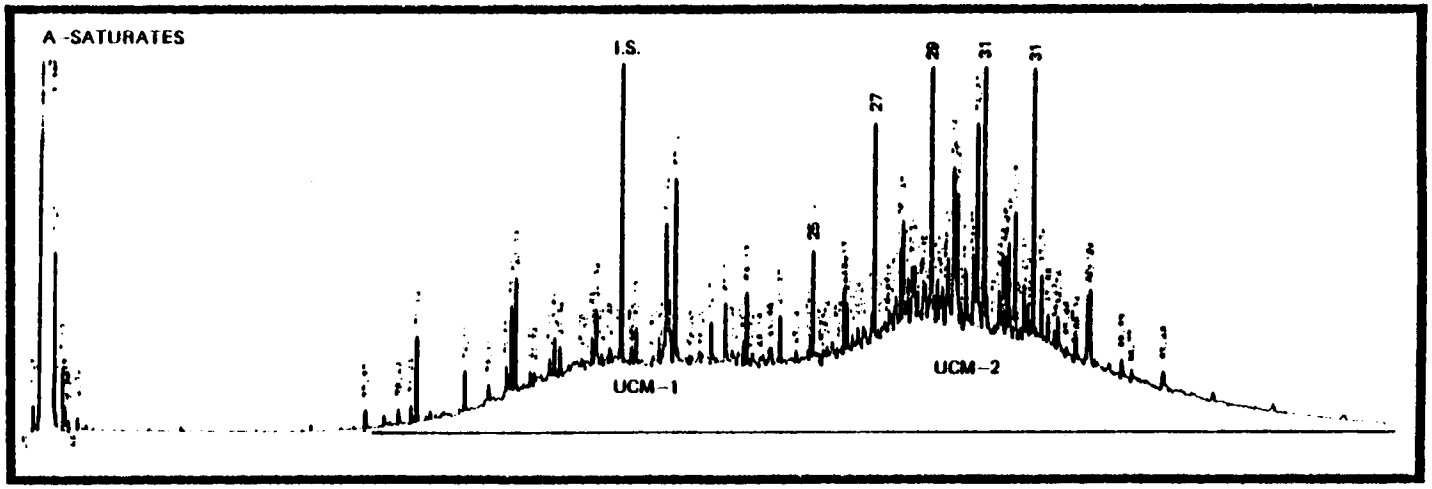


Figure 2–30. FSCGC Traces of Port Aransas Sediment Hydrocarbons.



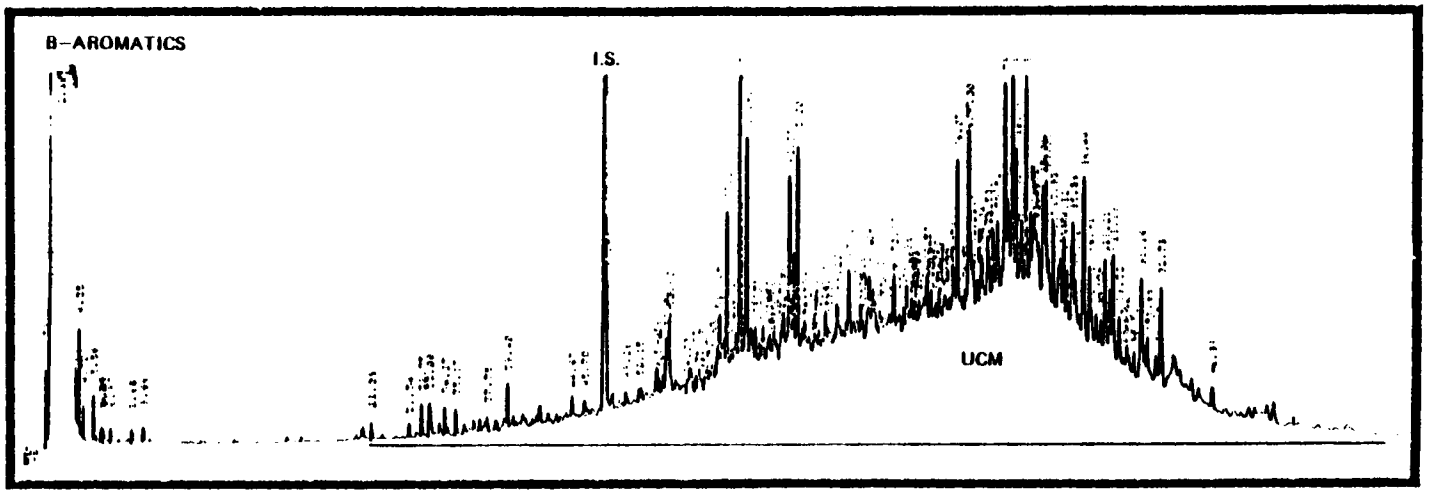


Figure 2–31. Typical South Texas OCS Hydrocarbon FSCGC Traces, (Station N–38, I–1, 1979).

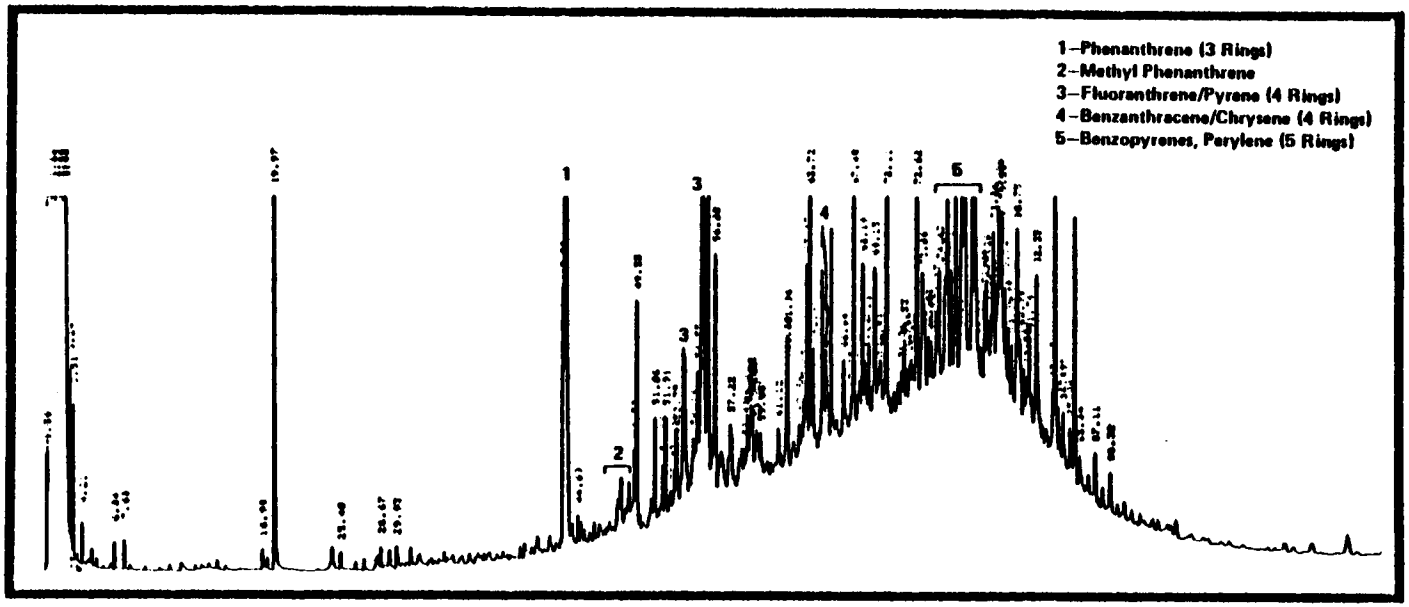


Figure 2–32. Capillary GC Trace of Aromatic Hydrocarbons in Texas OCS Intercalibration Sediment (Station II–2, M–36), Showing Pyrogenic PAH Inputs (See Section 2.3.2.3).

of petroleum-related hydrocarbons not attributable to either spill in question were detected by GC/MS analysis, as presented in Section 2.3.2.3.) Comparison of 1979 and 1980 FSCGC compositional data with the STOCS benchmark data (packed column GC) can be made through comparison of any or all of the parameter information derived from the FSCGC traces (see Table 2-14). However, most of these parameters rely heavily on the supposition that if oil were to impact the system, its n-alkane signature would be more or less intact. This is not the case as no obvious petrogenic n-alkane overprint of the sediment FSCGC traces was observed even in those samples in which petroleum was later detected (albeit not related to Ixtoc) through GC/MS analysis (see Section 2.3.2.3).

Nevertheless, as an academic exercise we have extracted data comparing n-alkane abundances in various boiling ranges (Tables 2-20, 2-21 and 2-22) and in total (Table 2-23), from available STOCS benchmark data and from the spill assessment data. Comparison of the n-alkane data through the various boiling ranges indicates that not only were a wide range of values found in the benchmark samples, but that almost always the 1979 and 1980 values fall within these ranges. The carbon preference index (CPI) and odd/even predominance (OEP) index, both measures of the contribution of petroleum alkanes to the background in the n-C_{25} to n-C_{32} region, are both consistently greater than 2.0 in all offshore sediment samples. CPI and OEP indices for petrogenic material are $\sim$1.0 indicating no odd or even carbon predominance. Thus CPI and OEP do not yield any indication of petroleum additions to the background, already dominated by terrigenous odd-carbon-number, high-molecular-weight alkanes.

Several typical saturated and aromatic hydrocarbon FSCGC traces are shown in Figures 2-30, 2-31, and 2-32. The saturated hydrocarbon traces reveal two major features: (1) a broad unresolved hump or unresolved complex mixture (UCM), and (2) a distribution of resolved components in the n-C_{22} to n-C_{32} range dominated by odd carbon chain n-alkanes, cyclic alkanes (naphthenes) and branched alkanes. The UCM is a characteristic chromatographic feature of weathered petroleum, urban air particulates, stormwater runoff, and the like (Farrington et al., 1976; Boehm, 1981), and is also a prominent feature observed in coastal marine sediments from many geographic regions. Its presence in sediments cannot be attributed to a particular spill without other evidence. Thus, in this case chronic anthropogenic inputs rather than recent spill inputs are responsible for the observed UCM. The odd chain n-alkanes are derived from waxy coatings on vascular land plants (Farrington et al., 1976).

The aromatic FSCGC traces also include unsaturated (olefinic) material as well. The trace shown in Figure 2-32 is typical of Gulf sediments (Gearing et al., 1976; Boehm and Fiest, 1980c) and consists mainly of (1) a UCM distribution related to chronic hydrocarbon inputs; (2) resolved olefinic material; and (3) polynuclear aromatic hydrocarbons (PAH) from a combustion (pyrogenic) source rather than a petroleum source (see Section 2.3.2.3 for a detailed discussion of PAH). Again, no traces of recent petroleum inputs can be seen. However, as will be seen, any recent low-level (ppb) inputs of petroleum will be detectable and identifiable in the aromatic fraction only

TABLE 2-20

SUMMARY OF "SUM LO" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE (all)	1979	1980	CHANGE[b]
M35	0.0	0.008	-	0.119	0.014	0.035	0.0 -0.119	0.041	0.013	N
M36	-	0.010	-	0.088	0.012	0.037	0.01 -0.09	0.056	0.028	N
M37	0.048	0.130	-	0.089	-	0.089	0.05 -0.13	0.037	0.027	N
N38	0.006	0.037	-	0.089	0.027	0.040	0.01 -0.09	0.068	0	N
N39	0.016	0.0	-	0.014	0.009	0.010	0.0 -0.02	0.033	0.021	N
N40	0.013	0.002	-	0.026	-	0.014	0.002-0.03	0.041	0.023	N
S49	-	0.032	0.133	-	0.015	0.060	0.02 -0.13	0.034	0.032	N
S50	0.013	0.011	0.031	-	-	0.018	0.01 -0.03	0.021	0	N
S51	-	0.063	0.068	-	-	0.065	0.06 -0.06	0.064	0.020	N
S52	0.024	0.053	0.006	-	0.085	0.042	0.01 -0.08	0.038	0.045	N
S53	0.010	0.009	0.027	-	-	0.015	0.01 -0.03	0.039	0.015	N
S54	0.0	0.006	0.059	-	-	0.022	0.0 -0.06	0.089	0.045	N

[a]SUM LO = sum n-alkanes from n-C_{14} to n-C_{18}.

[b]Based on comparison of 1979, 1980 values with STOCS range of values; N indicates no change.

TABLE 2-21

SUMMARY OF "SUM MID" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE(all)	1979	1980	CHANGE[b]
M35	0.06	0.03	-	0.09	0.04	0.055	0.03-0.09	0.290	0.050	(+)
M36	-	0.10	-	0.10	0.01	0.072	0.01-0.10	0.079	0.054	(N)
M37	0.02	0.52	-	0.11	-	0.286	0.02-0.52	0.151	0.115	(N)
N38	0.06	0.01	-	0.14	0.04	0.071	0.01-0.14	0.143	0.141	(N)
N39	0.13	0.002	-	0.02	0.01	0.017	0.002-0.13	0.094	0.078	(N)
N40	0.06	0.01	-	0.08	-	0.051	0.01-0.08	0.050	0.056	(N)
S49	-	0.04	0.26	-	0.07	0.124	0.04-0.26	0.029	0.158	(N)
S50	0.08	0.01	0.03	-	-	0.041	0.01-0.08	0.015	0.064	(N)
S51	-	0.14	0.15	-	-	0.146	0.14-0.15	0.103	0.093	(N)
S52	0.09	0.06	0.01	-	0.04	0.055	0.01-0.09	0.052	0.080	(N)
S53	0.05	0.02	0.02	-	-	0.031	0.02-0.05	0.047	0.034	(N)
S54	0.07	0.01	0.08	-	-	0.055	0.01-0.08	0.081	0.167	(+)

[a]SUM MID = sum n-alkanes from n-C_{19} to n-C_{24}.

[b]Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

TABLE 2-22

SUMMARY OF "SUM HI" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE(all)	1979	1980	CHANGE[b]
M35	0.77	0.05	-	0.50	0.47	0.44	0.05-0.77	0.757	0.270	N
M36	-	0.20	-	0.45	0.16	0.27	0.16-0.45	0.482	0.193	N
M37	0.64	0.73	-	0.57	-	0.65	0.57-0.73	0.637	0.442	N
N38	0.39	0.07	-	0.80	0.07	0.42	0.07-0.80	0.455	0.633	N
N39	0.51	0.01	-	0.15	0.08	0.22	0.01-0.51	0.476	0.384	N
N40	0.09	0.03	-	0.29	-	0.14	0.03-0.29	0.194	0.338	N
S49	-	0.56	1.2	-	1.2	0.99	0.6 -1.2	0.022	0.590	N
S50	0.12	0.01	0.10	-	-	0.08	0.01-0.12	0.023	0.474	N
S51	-	0.92	0.97	-	-	0.93	0.92-0.97	0.457	0.377	N
S52	0.36	0.13	0.03	-	0.35	0.17	0.03-0.36	0.107	0.258	N
S53	0.13	0.02	0.08	-	-	0.08	0.02-0.13	0.155	0.112	N
S54	0.14	0.04	0.43	-	-	0.2	0.04-0.43	0.306	0.462	N

[a]SUM HI = sum n-alkanes from n-C_{25} to n-C_{32}.

[b]Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

TABLE 2-23

SUMMARY OF TOTAL N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS

	STOCS BASELINE DATA								DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{X}$(all)	RANGE (all)	$\bar{X}^a$	1979	1980	CHANGE[b]
M35	0.83	0.09	-	0.70	0.53	0.54	0.09-0.83	0.77	1.090	0.337	N
M36	-	0.31	-	0.64	0.19	0.38	0.19-0.64	0.64	0.617	0.274	N
M37	0.92	1.4	-	0.77	-	1.02	0.77-1.4	0.85	0.826	0.584	N
N38	0.46	0.18	-	1.0	0.14	0.45	0.18-1.0	0.53	0.666	0.774	N
N39	0.66	0.01	-	0.18	0.10	0.24	0.01-0.66	0.31	0.603	0.483	N
N40	0.16	0.04	-	0.39	-	0.20	0.04-0.39	0.27	0.285	0.417	N
S49	-	0.64	1.6	-	1.3	1.2	0.64-1.6	-	0.085	0.781	N
S50	0.22	0.03	0.16	-	-	0.14	0.03-0.22	0.22	0.060	0.538	N
S51	-	1.1	1.2	-	-	1.2	1.1 -1.2	-	0.623	0.490	N
S52	0.47	0.24	0.05	-	0.47	0.31	0.05-0.47	0.47	0.197	0.383	N
S53	0.19	0.45	0.13	-	-	0.26	0.13-0.45	0.19	0.242	0.161	N
S54	0.21	0.05	0.57	-	-	0.27	0.05-0.57	0.21	0.475	0.674	N

[a]Fall/winter values only.

[b]Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

through GC/MS investigation. On a grosser level (ppm), although petroleum parameters cannot be seen in the sediment through evaluation of the FSCGC traces, the combustion-related PAH are quite evident in most samples.

The collection of six sediment samples from the Burmah Agate site were analyzed similarly by FSCGC. Hydrocarbon concentrations in these samples ($f_1 + f_2$) ranged from 8 to 75 ppm ($\bar{x} = 29.5 \pm 24.5$). The samples, which were not subjected to UV/F, contained large quantities of UCM material which account for most of the differences in concentration between these samples and those of the main study area. The total n-alkane concentrations in these samples fell well within those from further south, thus again illustrating the lack of usefulness of n-alkanes in spill assessments of this type. Three of the Burmah Agate sediment samples do contain aromatic residues of the Burmah Agate oil, as will be seen in the next section (Stations G02, G04 and G05). Stable isotope measurements (Section Three) confirm the presence of Burmah Agate oil residues in one of the samples and give ambiguous results on the others. Representative FSCGC traces (Figure 2-33) of a sediment sample from station G02 illustrates the large UCM (bimodal) in both f_1 and f_2 fractions but gives little indication of the source of the PHC residues.

Five samples taken further offshore in deeper water (see Figure 2-6) from the 1979 Antelope collection were analyzed by FSCGC as well. These samples ranged in PHC concentration from 8 to 15 ppm. No recent oil additions are evident from the FSCGC traces. An interesting group of compounds appears later in the f_2 GC trace. These are believed to be sterenes and triterpenes of a biogenic origin, although further GC/MS confirmation is needed.

The series of Researcher/Pierce samples from south of the study area (Figure 2-6) examined by FSCGC revealed levels of hydrocarbons in the 3-25 ppm range with concentrations increasing offshore. However, no relation to any spillage event was discerned in the FSCGC traces; normal geochemical inputs are responsible for the observed distributions.

2.3.2.3 Aromatic Hydrocarbons by GC/MS

All polynuclear aromatic hydrocarbons that were detected in the Ixtoc I oils were again sought in the sediment extracts. These data are presented in detail in Appendix 9.1. The concentrations of individual petroleum aromatic compounds (two and three rings) are most often in the low ppb range while the pyrogenic PAH are present at higher concentrations. Similar information is not available from the STOCS program.

In most of the sediment samples, significant amounts of alkylated phenanthrenes and alkylated dibenzothiophenes were not found. As these compounds are the major diagnostic molecular markers of crude oils, this finding rules out widespread Ixtoc I or Burmah Agate petrolem inputs to the sediments. In some cases only the mono- and dialkylated phenanthrenes and

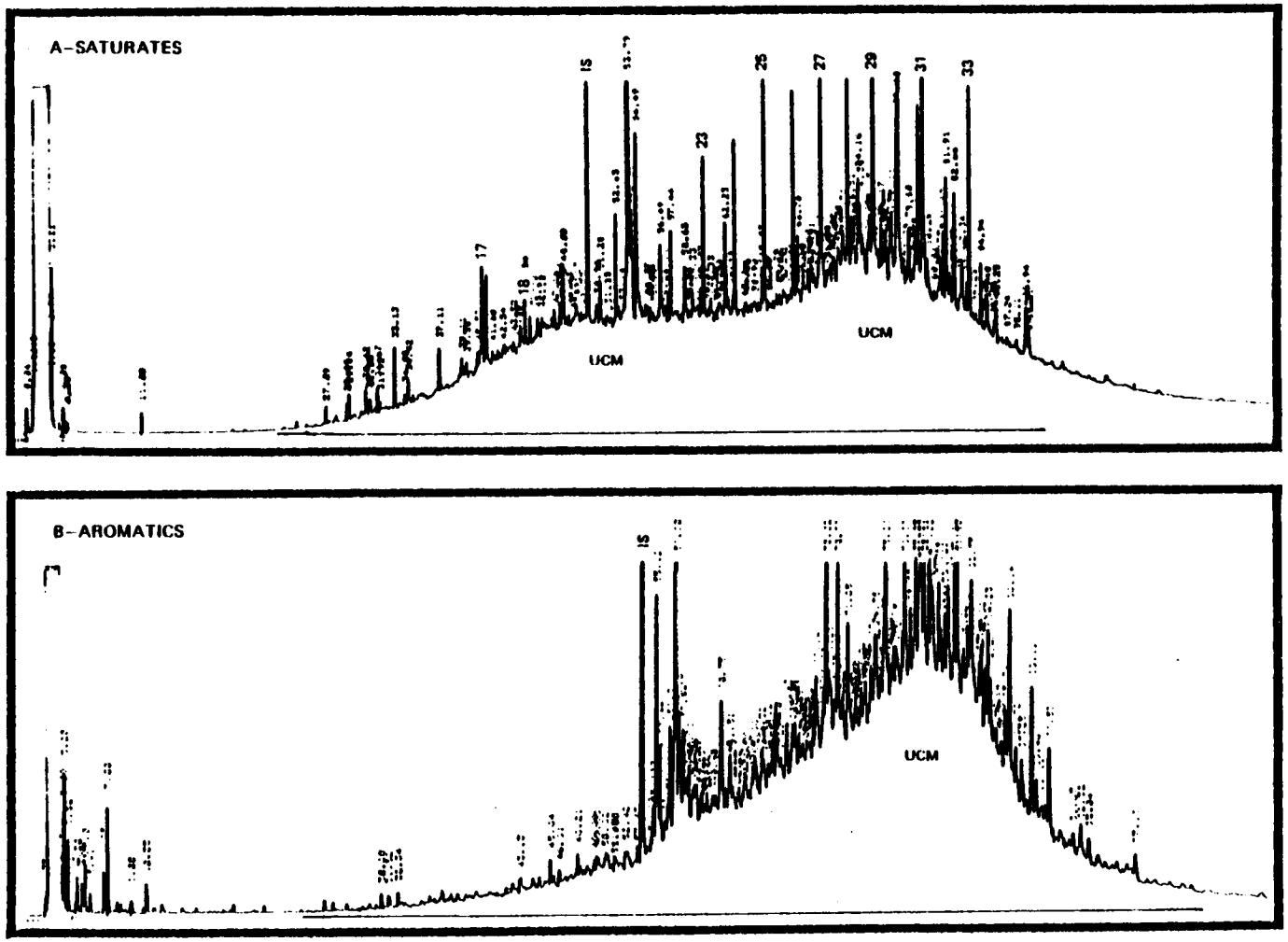


Figure 2–33. Representative FSCGC Traces of Burmah Agate Impact Area Sediments (Station G 02).

dibenzothiophenes were detected. In these cases, attempts to match these aromatic compounds with a source fail primarily because the C_1P/C_1DBT ratio is not reliable due to weathering effects (Table 2-24) and the presence of the C_3 homologs is essential to establish a match. The few sediments which did contain the complete series of alkyl phenanthrenes and alkyl dibenzothiophenes (e.g., NO_3, NO_4; Table 2-24) had C_1, C_2, and C_3 homologue ratios decidedly higher than either the Burmah Agate or Ixtoc I oils (see Table 2-24). The presence of these aromatics in these samples may be attributable to low levels of an unknown source of petroleum and to pyrolytic inputs. The high ratios of phenanthrenes to dibenzothiophenes are due to phenanthrene inputs attributable to combustion (i.e., pyrolytic inputs). Three sediment samples collected in the area of the Burmah Agate spill were found to contain petrogenic aromatics. C_2 and C_3 alkyl phenanthrene-alkyl dibenzothiophene ratios compare favorably with those values found for Burmah Agate oils. C_1 ratios were slightly higher for the sediment samples than the oil samples, which is probably attributable to weathering effects. One sediment sample shown to be contaminated with oil (Port Aransas sample - PA2) showed C_1, C_2, and C_3 alkyl phenanthrene-dibenzothiophene ratios nearly identical to those found for moderately weathered Ixtoc I oil. However, this sample is taken from a heavily used port area so attributing the aromatics in this sample to Ixtoc I oil has some uncertainty.

Significant quantities of nonalkylated PAH were found in many of the sediments. These compounds include phenanthrene (m/e = 178), pyrene (m/e = 202), fluoranthene (m/e = 202), benzanthracene and chrysene (m/e = 228), benzopyrene isomers (m/e = 252), and perylene (m/e = 252). Concentrations of phenanthrene ranged from <0.1 $ng \cdot g^{-1}$ to 25 $ng \cdot g^{-1}$, fluoranthene-pyrene from 0.1 $ng \cdot g^{-1}$ to 96 $ng \cdot g^{-1}$, benzo(a)anthracene-chrysene from <0.1 $ng \cdot g^{-1}$ to 44 $ng \cdot g^{-1}$, benzofluoranthene-benzo(a)pyrene-benzo(e)pyrene from <0.1 $ng \cdot g^{-1}$ to 91 $ng \cdot g^{-1}$ and for perylene from <0.1 $ng \cdot g^{-1}$ to 123 $ng \cdot g^{-1}$. The predominance of these nonalkylated PAH compounds suggests pyrogenic sources (e.g., combustion of fossil fuels), not petroleum contamination (Youngblood and Blumer, 1975). Their presence in these sediments is probably a result of atmospheric fallout and terrestrial runoff, part of the usual pollutant depositional environment of the region.

Concentration profiles of each of the pyrogenic PAH are mapped in Figures 2-34 to 2-38. In each survey the quantities of pyrogenic PAH were greater in offshore (>25 m depth) than in near-shore (<25 m depth) samples. This seems to correlate well with total organic carbon (TOC) data derived for many of the sediments. This is demonstrated in Figures 2-39 to 2-41 where TOC values have been compared with representative pyrogenic PAH (benz[a]-anthracene-chrysene, fluoranthene, pyrene, perylene) from the 1980 survey. The reason for this is that near-shore sediments typically contain coarser sediment particles than do deep-sea sediments. Concentrations of lipids are usually higher in finer-grained sedimentary material (Thompson and Eglinton, 1978) found in depositional environments. These areas are also better suited for net deposition of fine-grained pyrogenic residues (i.e., soot).

TABLE 2-24

GC/MS-DETERMINED SEDIMENT ALKYL PHENANTHRENE/ ALKYL DIBENZOTHIOPHENE RATIOS

STATION	YEAR	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT	SOURCE[a]
STOCS Stations:					
S53	1979	8.00	2.50	0.73	P/U
N39	1979	22.5	8.67	20.0	P/U
S51	1980	12.5	5.80	-	P/U
S52	1980	5.18	4.60	-	P/U
N40	1980	21.0	4.50	-	P/U
S49	1980	19.8	8.00	-	P/U
N03	1980	15.7	5.74	2.43	P/U
N04	1980	30.2	8.59	5.68	P/U
Burmah Agate Stations:					
G04	1980	9.75	6.23	9.58	BA
G02	1980	7.78	3.70	3.26	BA
G05	1980	8.65	3.40	5.75	BA
Port Aransas:					
PA2	1979	1.50	0.53	0.72	I
Range of Ixtoc Oils:		0.72-1.32	0.41-0.66	0.49-0.80	
Range of Burmah Agate Oils:		3.56-5.09	3.41-5.11	5.36-11.36	

[a]P/U = combined source of pyrolytic combustion aromatics and lesser amounts of unidentified chronic petroleum source.

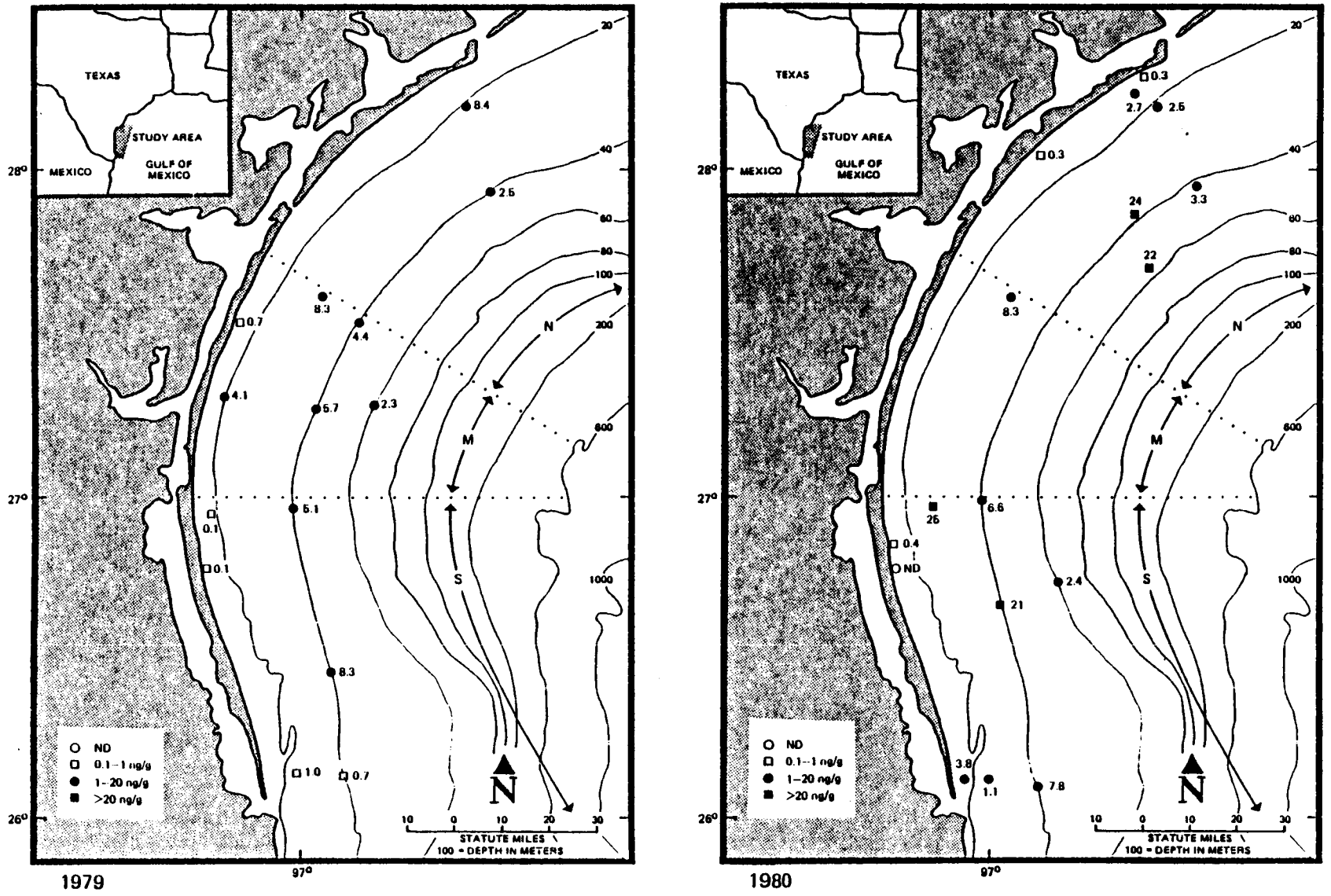


Figure 2–34. Phenanthrene Concentrations in Sediments (ng/g).

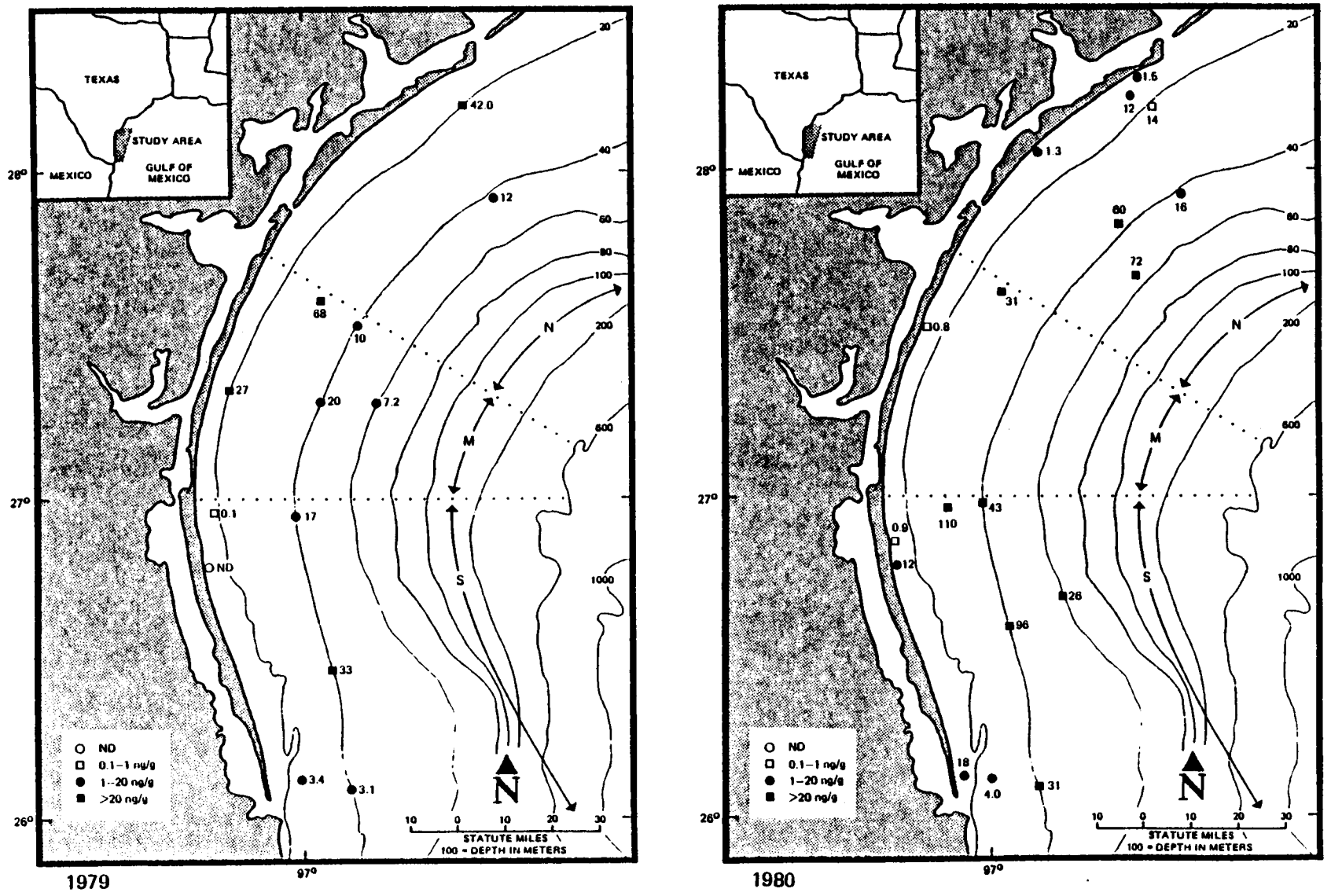


Figure 2–35. Fluoranthene/Pyrene Concentrations in Sediments (ng/g).

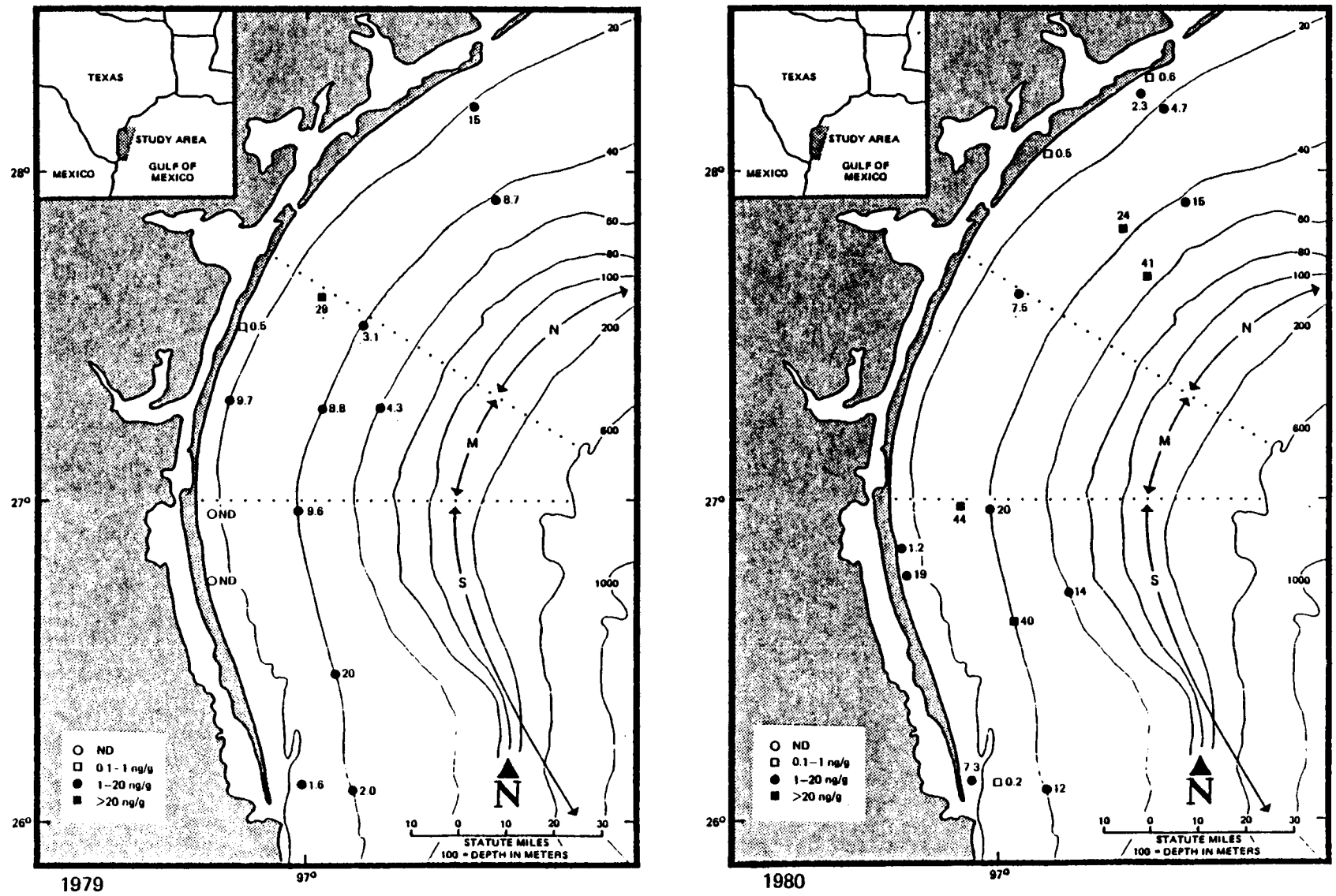


Figure 2–36. Benzanthracene/Chrysene Concentration in Sediments (ng/g).

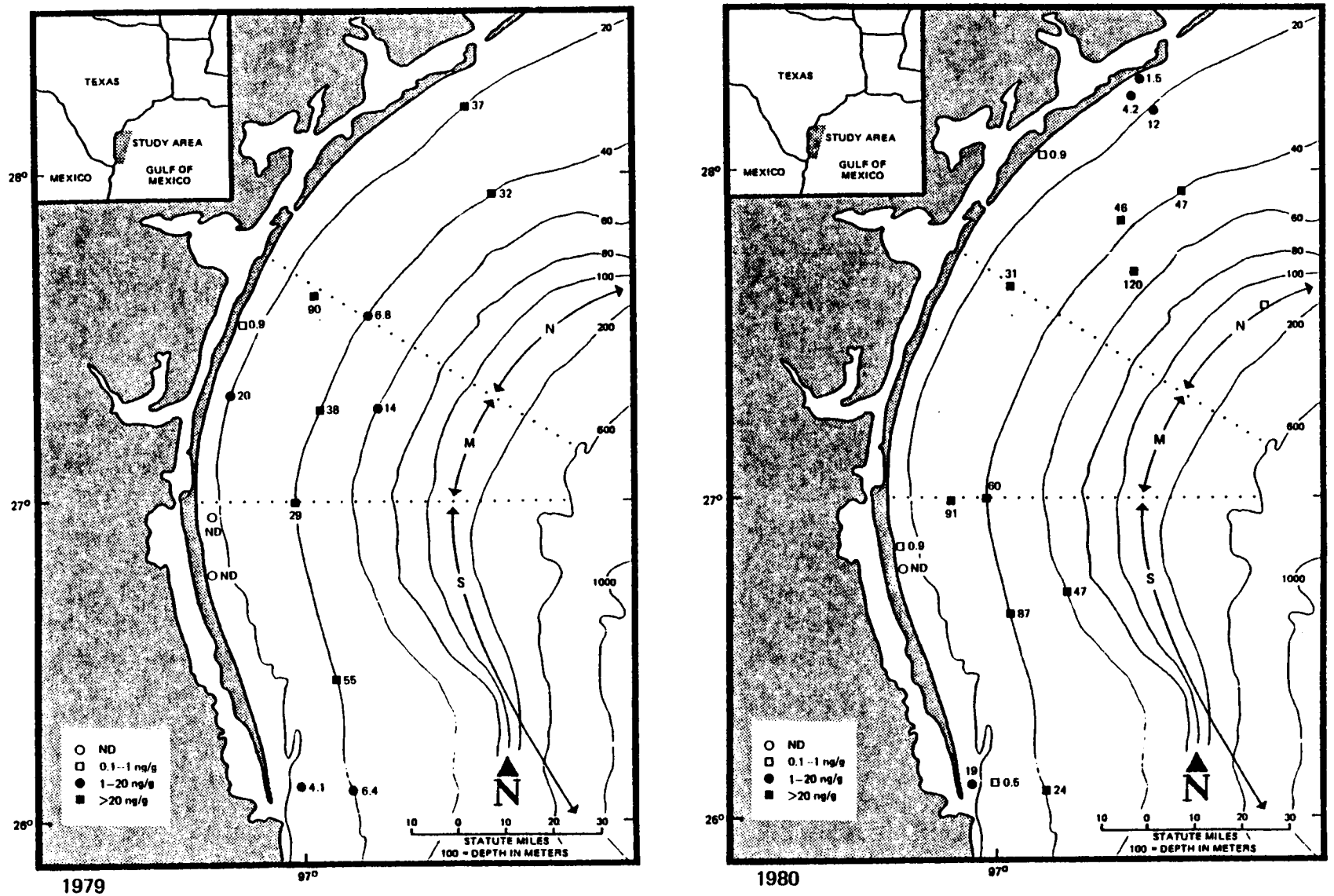


Figure 2–37. Benzofluoranthene / Benzo (a)Pyrene / Benzo(e)Pyrene Concentrations in Sediments (ng/g).

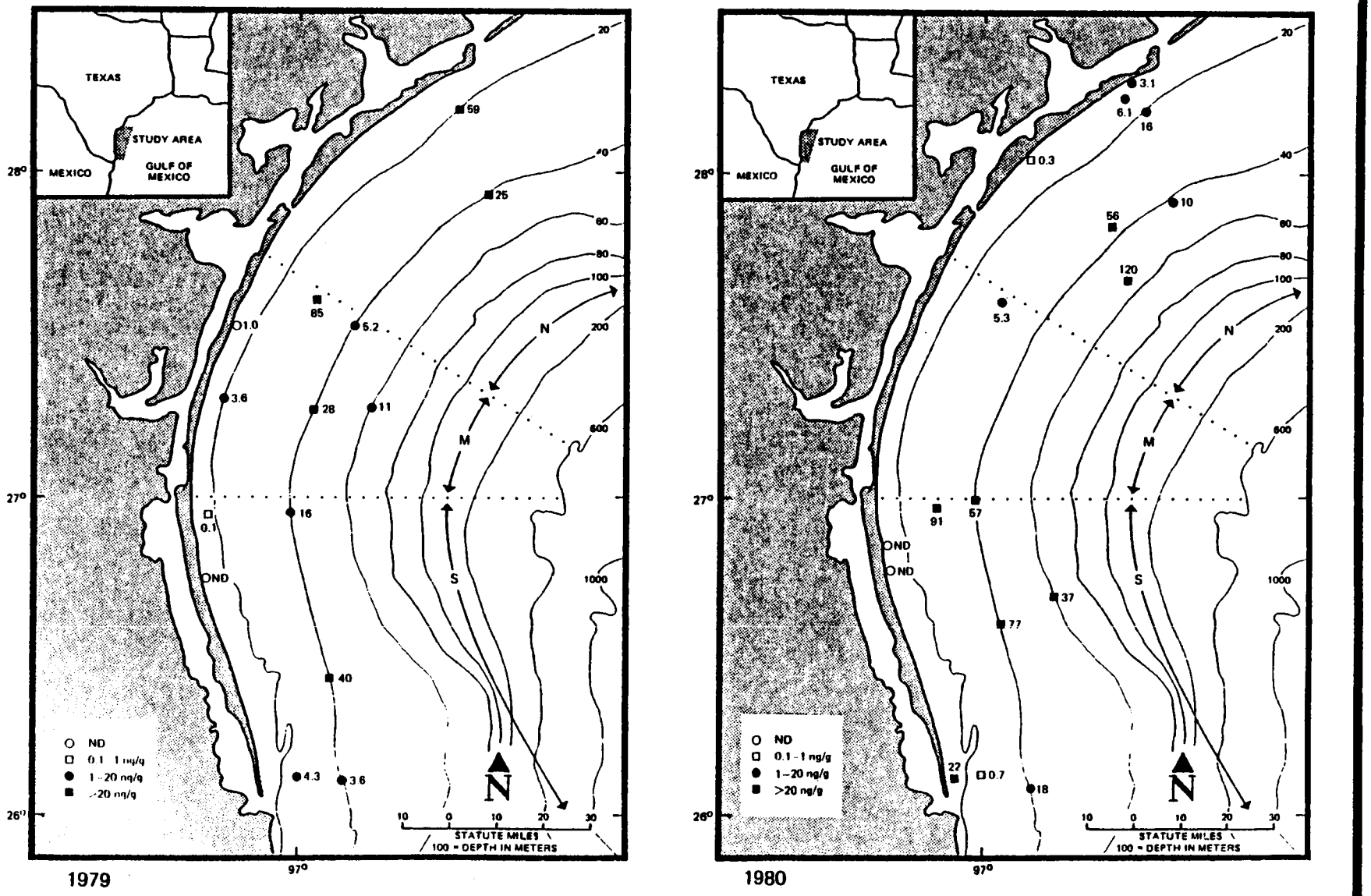


Figure 2–38. Perylene Concentrations in Sediments (ng/g).

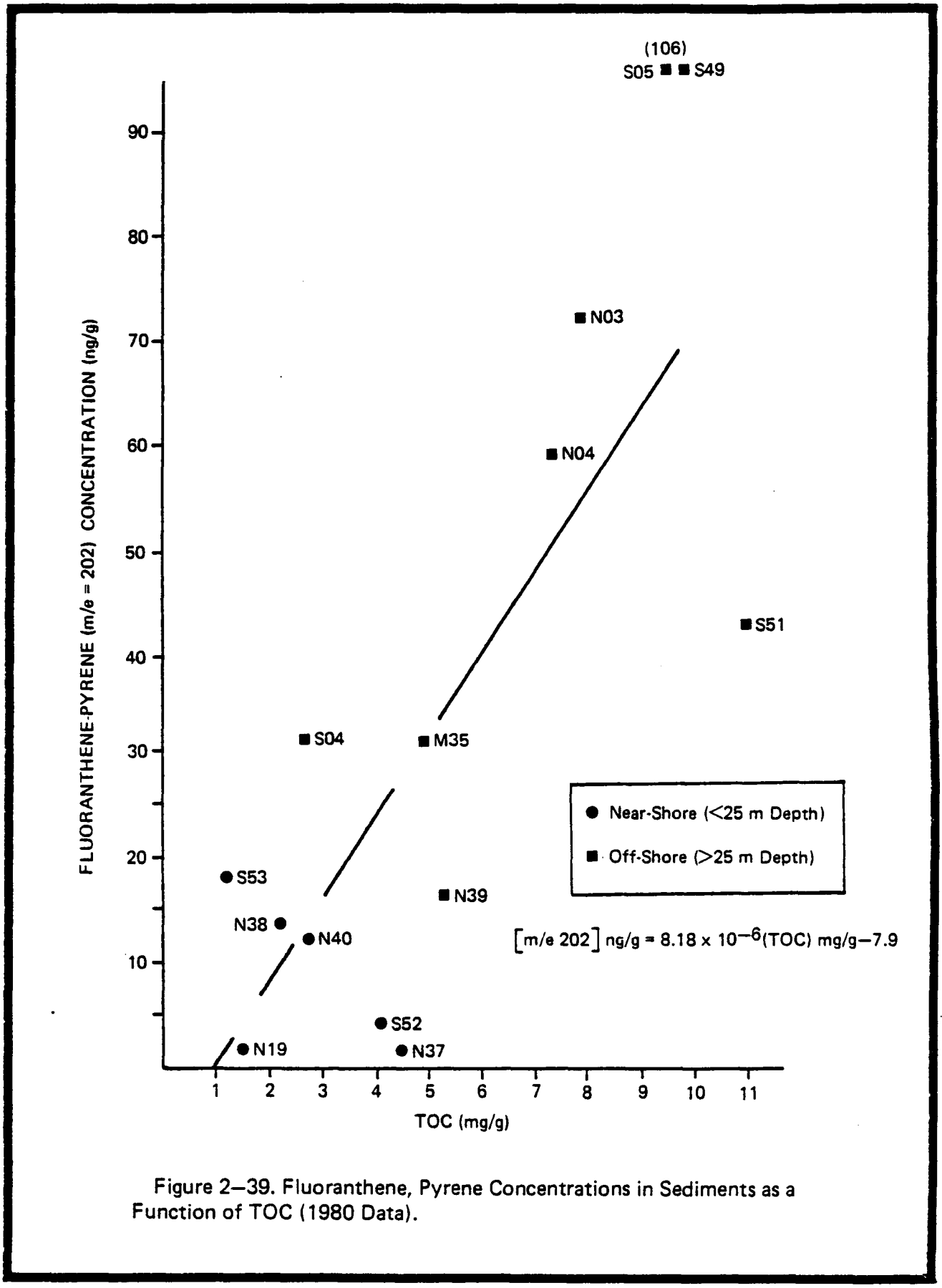


Figure 2–39. Fluoranthene, Pyrene Concentrations in Sediments as a Function of TOC (1980 Data).

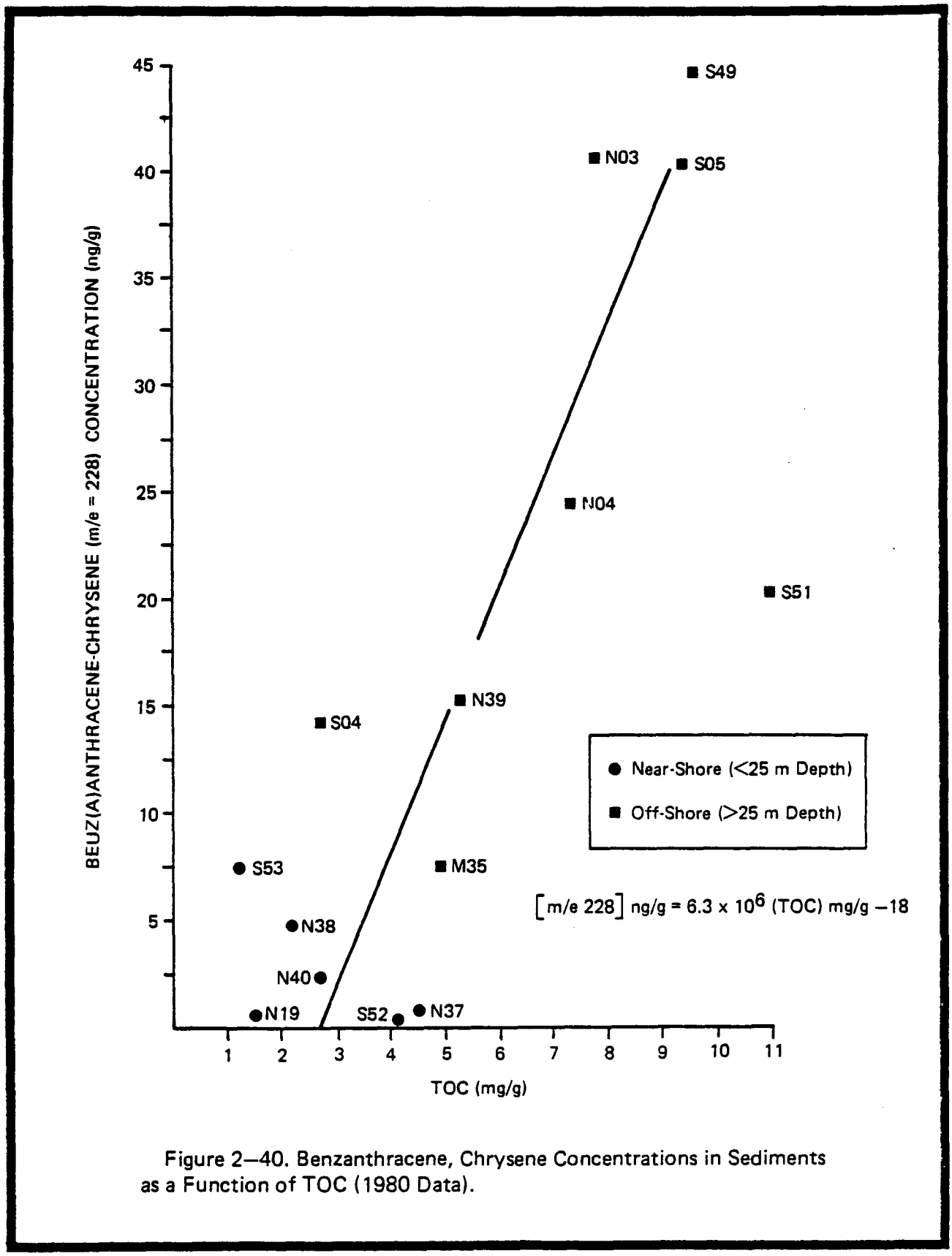


Figure 2—40. Benzanthracene, Chrysene Concentrations in Sediments as a Function of TOC (1980 Data).

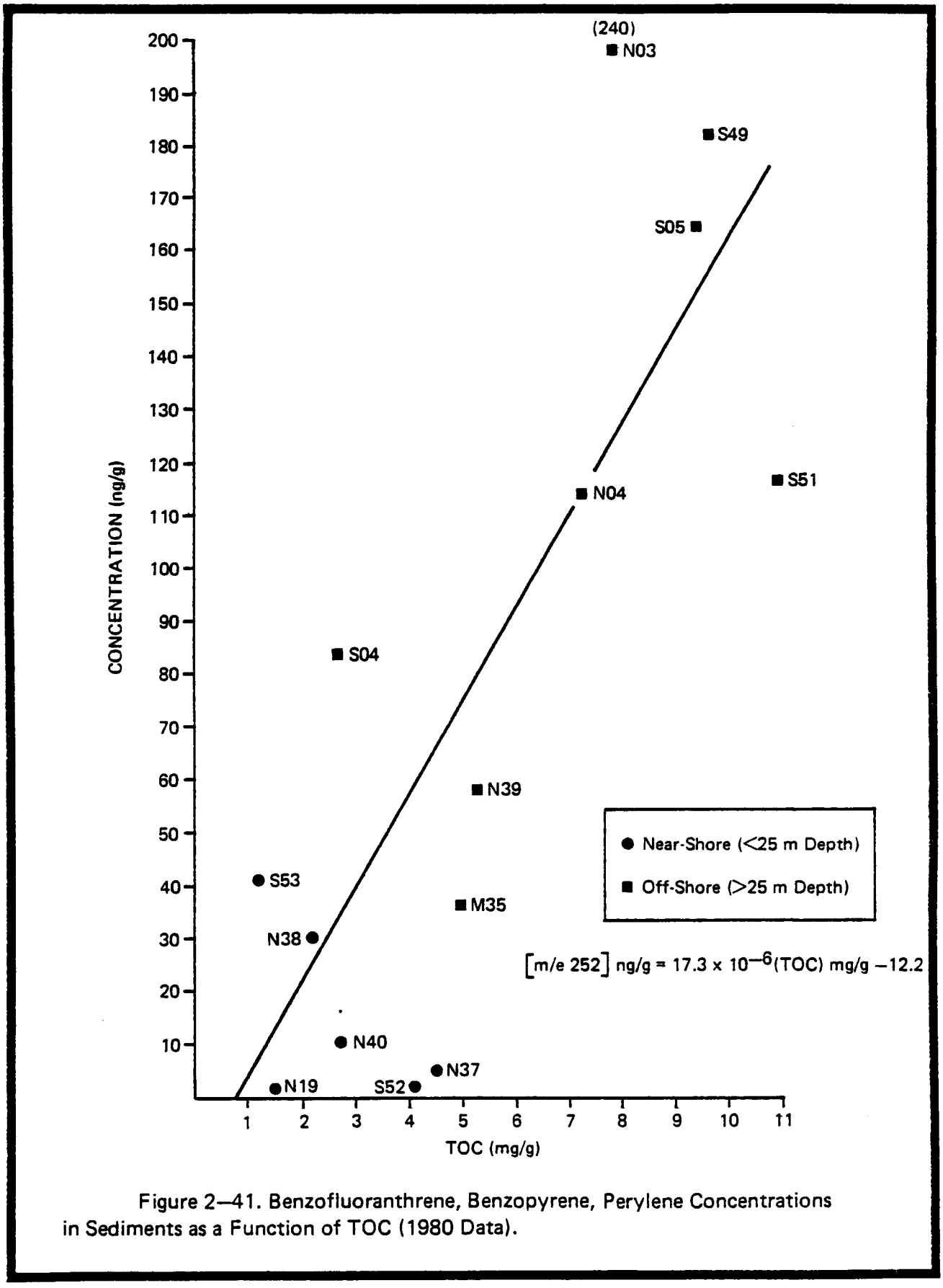


Figure 2–41. Benzofluoranthrene, Benzopyrene, Perylene Concentrations in Sediments as a Function of TOC (1980 Data).

A comparison of pyrogenic PAH concentrations has been made for coinciding 1979 and 1980 survey sites (Table 2-25). Although quantities were generally comparable, at sites N38, M35, and S52, 1979 PAH concentrations were higher by as much as two to three times the levels found in the 1980 samples. At sites N39, S51, and S31, 1980 values were slightly higher than 1979 values. Only at site S54 were values substantially different, with some concentrations being 10 times greater in the 1980 survey. An overall impression of these comparisons is that pyrogenic PAH levels have been fairly stable over a 1-year period, with no dramatic impact or degradation of these compounds apparent. Variations found can be explained by normal geochemical variability. For example the TOC levels at Station S54 increased from 4.7 to 10.6 and the total PHC levels from 9.8 to 17.5 between 1979 and 1980. As pyrogenic PAH would be associated with fine soot-like particles, this large TOC increase (6 $mg \cdot g^{-1}$) could have presumably included small amounts of soot-bearing PAH at the 50-100 $ng \cdot g^{-1}$ level. If one considers historical data available from Laseter and Overton (undated) (Table 2-26) then a remarkable stability in PAH levels is seen. These data are unique in that they not only combine temporal geochemical information but interlaboratory-derived results as well.

The precision of the GC/MS analyses on two subsamples of a sediment sample from Station S04 is excellent (coefficients of variation for individual PAH $\leq$20%), thus precluding analytical variability or subsampling variability in accounting for seasonal PAH changes (see Section 2.2.5).

2.3.3 Petroleum Hydrocarbons in Sorbent Pads

2.3.3.1 FSCGC Analysis

The sorbent pad samples captured a nonquantitative sample of subsurface particulate material potentially including suspended sediment and particulate oil residues. The aim of this sampling was to obtain subsurface oil residues and recently deposited (and then resuspended) particulate matter.

As much of the material in the samples was (possibly resuspended) sediment, concentrations of PHC were calculated on a dry-weight-of-sediment basis and are presented in Table 2-27. As indicated by the CPI values and as seen in the FSCGC traces (e.g., Figures 2-42 and 2-43), the sample obtained is most often a mixture of relatively recent petroleum input and background material. CPI values range from 1.2 to 8.0. Hydrocarbons in those samples having CPI values between 1.0 and 1.5 have been classified as primarily oil-derived. Terrigenous plant material and chronic anthropogenic input to the samples will increase the CPI. For example, the sample taken at Station N26 is predominantly background geochemical material.

The FSCGC traces indicate that the sorbent pads are significantly different from the surficial sediments in composition. The pads are in most cases characterized by a petroleum-related hydrocarbon assemblage combined with a sedimentary source, the latter signified by the terrigenous odd-carbon chain n-alkane ($n\text{-}C_{23}$ to $n\text{-}C_{33}$) distribution. It is significant to note that the sorbent pad samples from the southern sector ("S" stations)

TABLE 2-25

COMPARISON OF PYROGENIC PAH AT STATIONS SAMPLED IN BOTH FROM THE 1979 AND 1980 SURVEYS

		CONCENTRATIONS ($ng \cdot g^{-1}$)				
SITE	SURVEY	PHEN.	FLUOR.-PYR.	BENZ.-CHRY.	BENZO PYRENES	PERYLENE
N38	1979	8.4	42.0	15.2	36.9	59.2
	1980	2.5	13.8	4.7	12.5	16.5
N39	1979	2.5	12.2	8.7	31.9	24.7
	L980	3.3	15.9	15.3	47.5	10.0
M35	1979	8.3	68.3	28.9	90.2	84.9
	1980	8.3	30.8	7.5	30.5	5.3
S51	1979	5.1	17.1	9.6	29.0	16.0
	1980	6.6	42.9	20.2	59.5	57.1
S31	1979	0.1	ND	ND	ND	ND
	1980	ND	11.6	19.4	ND	ND
S52	1979	1.0	3.4	1.6	4.1	4.3
	1980	1.1	4.0	0.2	0.5	0.7
S54	1979	0.7	3.1	2.0	6.4	3.6
	1980	7.8	31.3	11.8	23.6	17.8

PHEN = Phenanthrene
FLUOR = Fluoranthrene
PYR = Pyrene
BENZ = Benzanthracene
CHRY = Chrysene

TABLE 2-26

COMPARISON OF SELECTED AROMATIC COMPOUND CONCENTRATIONS WITH HISTORICAL DATA

(Concentration: $ng \cdot g^{-1}$)

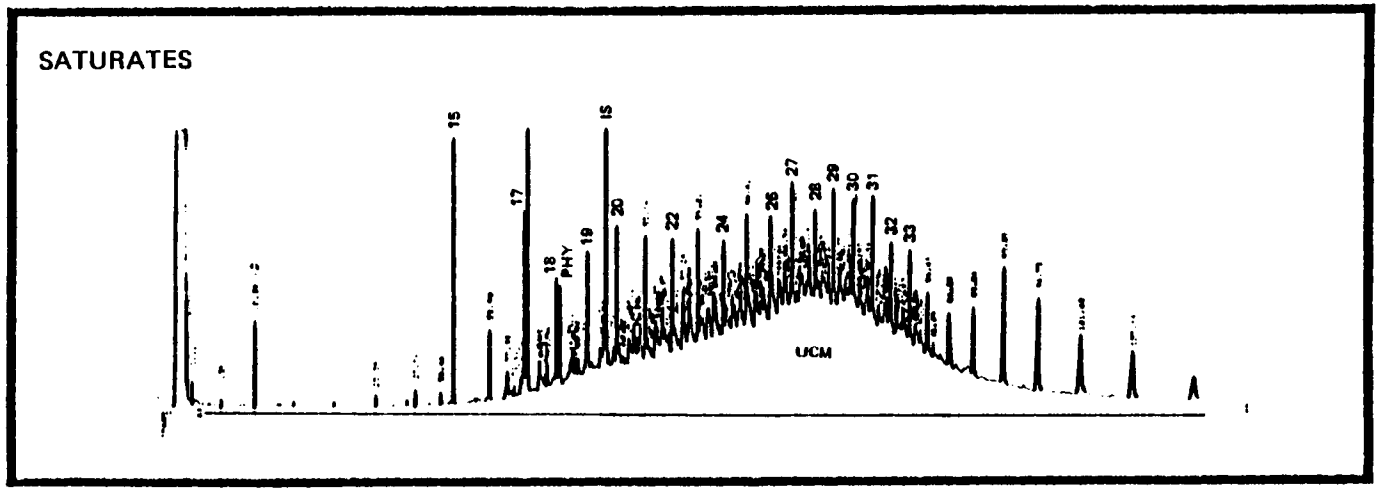
COMPOUND	STOCS STATION	1976 (1977) STUDY[a]	1979 STUDY	1980 STUDY
2-Methyl Naphthalene	M36	2.3	-	1.3
	S52	0.8 (Tr)	0.4	0.2
	S53	0.6	-	0.9
	N38	0.4	-	1.5
1-Methyl Naphthalene	M36	2.0	-	0.5
	S52	0.5 (Tr)	0.2	0.1
	S53	Tr	-	0.2
	N38	Tr	ND	ND
Fluoranthene	M36	7.0	-	17
	S52	3.2 (1.8)	1.3	1.6
	S53	1.9	-	7.3
	N38	4.9	15	4.9
Pyrene	M36	5.8	-	18.0
	S52	4.8 (2.9)	2.1	2.4
	S53	6.3	-	10
	N38	7.9	27	8.9
Chrysene	M36	5.5	-	11.0
	S52	4.9 (1.6)	1.0	0.1
	S53	2.0	-	3.7
	N38	5.3	9.6	2.4

[a]Laseter and Overton, undated.

TABLE 2-27

SORBENT PAD HYDROCARBON DATA SUMMARY

STATION	f_1 ($\mu g \cdot g^{-1}$)	f_2 ($\mu g \cdot g^{-1}$)	PRIS/ $n \cdot C_{17}$	PHY/ $n \cdot C_{18}$	PRIS/ PHY	CPI	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT	SOURCE
S27	177	108	2.8	1.5	2.4	1.2	7.30	0.66	0.26	oil
S15	165	107	3.5	2.1	7.2	2.5	-	-	-	oil/background
N26	125	79	1.7	0.5	5.1	8.0	-	-	-	background
N27	442	354	0.6	0.9	2.2	1.9	-	-	-	background/oil
S46	225	159	3.1	1.0	5.5	1.3	4.59	0.78	0.80	oil
M25	215	410	1.0	0.8	1.1	1.9	-	0.57	0.40	background/oil
M26	98	164	1.0	0.6	2.1	1.7	-	-	-	background
N20	140	74	5.0	0.5	9.4	1.8	-	-	-	background/oil
S21	86	64	0.8	0.9	3.1	1.3	2.83	0.62	0.74	oil
Range of Ixtoc I oils							.72-1.32	.41-.66	.49-.80	



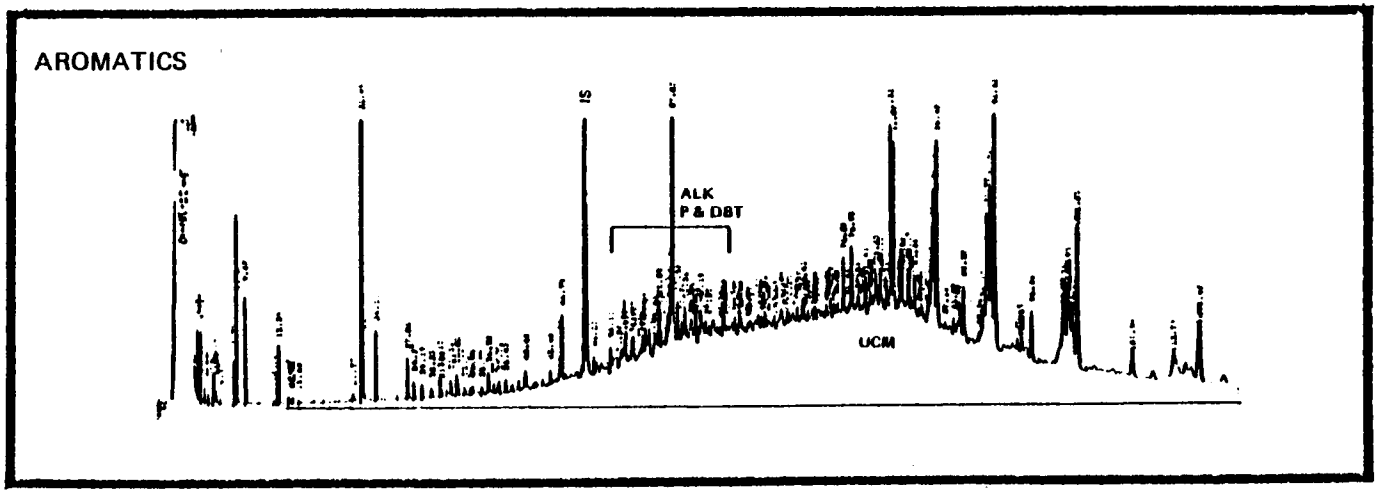
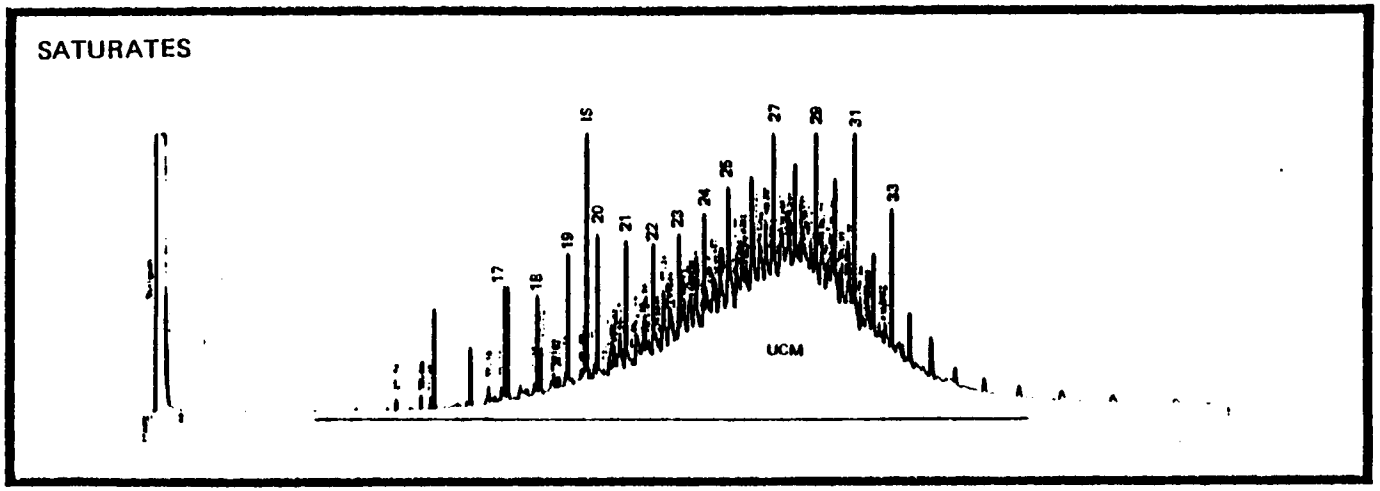


Figure 2–42. FSCGC Traces of Sorbent Pad Hydrocarbons–Station S46.



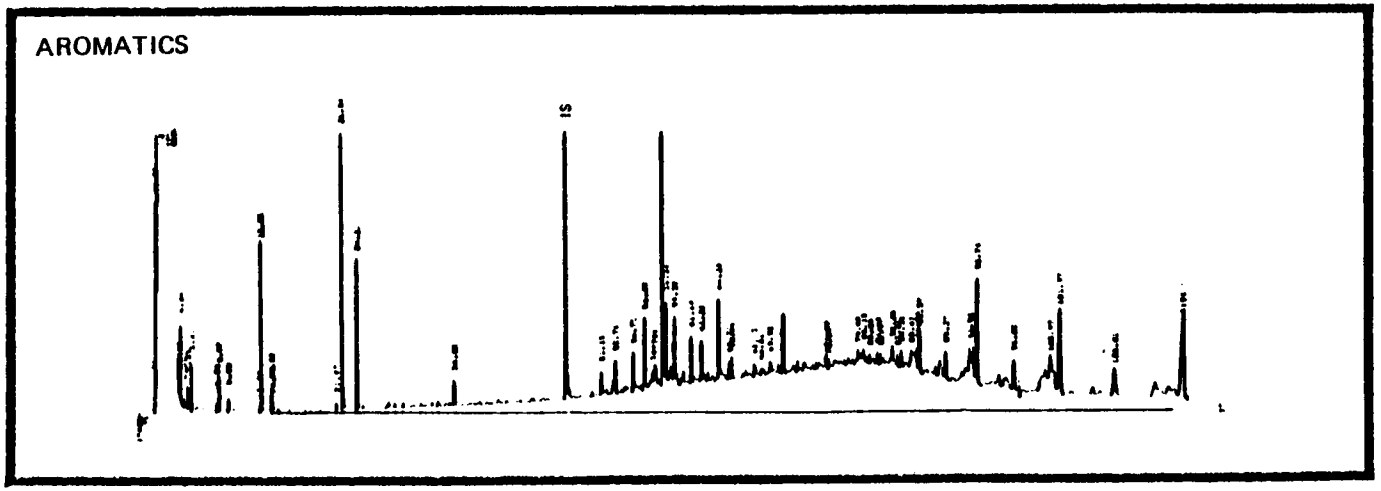


Figure 2–43. FSCGC Traces of Hydrocarbons in Sorbent Pad (Station M–26).

consistently exhibit oil residues in the FSCGC traces (e.g., Figure 2-42) while the "N" and "M" stations contain largely background hydrocarbon material. When n-alkane comparisons are used to match sorbent pad residues with Ixtoc oil (Figure 2-44), the mixed source inputs become apparent and the use of n-alkane source matching becomes difficult. Even in samples largely dominated by oil residues (see next section) the presence of disproportionate quantities of n-C_{15} and n-C_{17}, both of phytoplanktonic origin, and n-C_{25} through n-C_{29}, of terrigenous plant origin, overprints the petroleum fingerprint. By tradition, the use of pristane and phytane ratios, to each other and to the adjacent n-alkanes (Table 2-14) have been used to distinguish oil from biogenic material. While all four components are present in oil, initially with PRIS/PHY $\sim$1 and PRIS/n-C_{17} and PHY/n-C_{18} both less than 1, inputs of n-C_{17} from phytoplankton and pristane from zooplankton obscure the ability of these ratios to establish the presence of weathered oil residues.

2.3.3.2 Aromatic Hydrocarbons by GC/MS

The examination of four representative sorbent pad samples by GC/MS yielded the aromatic data presented in Appendix 9.1. Levels of individual Group I (two and three rings) aromatics ranged from nd to 140 $ng \cdot g^{-1}$ with maximum concentrations for the alkylated phenanthrene and dibenzothiophene compounds. Sourcing of these apparent petrogenic residues by ratios of these alkylated compounds indicates a strong relation to Ixtoc oil in the C_2 and C_3 ratios (Table 2-27). Stable isotope data on the S21 and S46 samples confirm this probable identification.

Group II PAH levels in these samples are low (1-30 $ng \cdot g^{-1}$) indicating that the aromatic assemblage is not strongly petrogenic. Rather, taken together, the high Group I levels and low Group II levels indicate a strongly petrogenic source of the aromatic assemblage in the sorbent pad samples. This is quite a different result from that found for the surface sediments where the aromatic assemblage was found to be highly pyrogenic.

2.3.4 Petroleum Hydrocarbons in Macroepifauna (Penaeid Shrimp)

Seventy samples of penaeid shrimp obtained from the 1979 Western Gulf, Longhorn IV and dockside shrimp collections and forty-one 1980 samples were considered in this study (see Figure 2-5 and Table 2-4 for locations).

2.3.4.1 UV/F Screening

Solvent extracts of all samples were analyzed by synchronous and fixed-excitation UV/F to enable a selection of samples to be made for subsequent more detailed analysis. Several experiments were performed prior to the analysis of the entire sample set. These experiments explored: (1) the quenching of the spectral bands by the tissue extract matrix (high lipid content), (2) the threshold detection level of oil based on incremental oil additions to shrimp UV/F background, and (3) the additivity of spectral response.

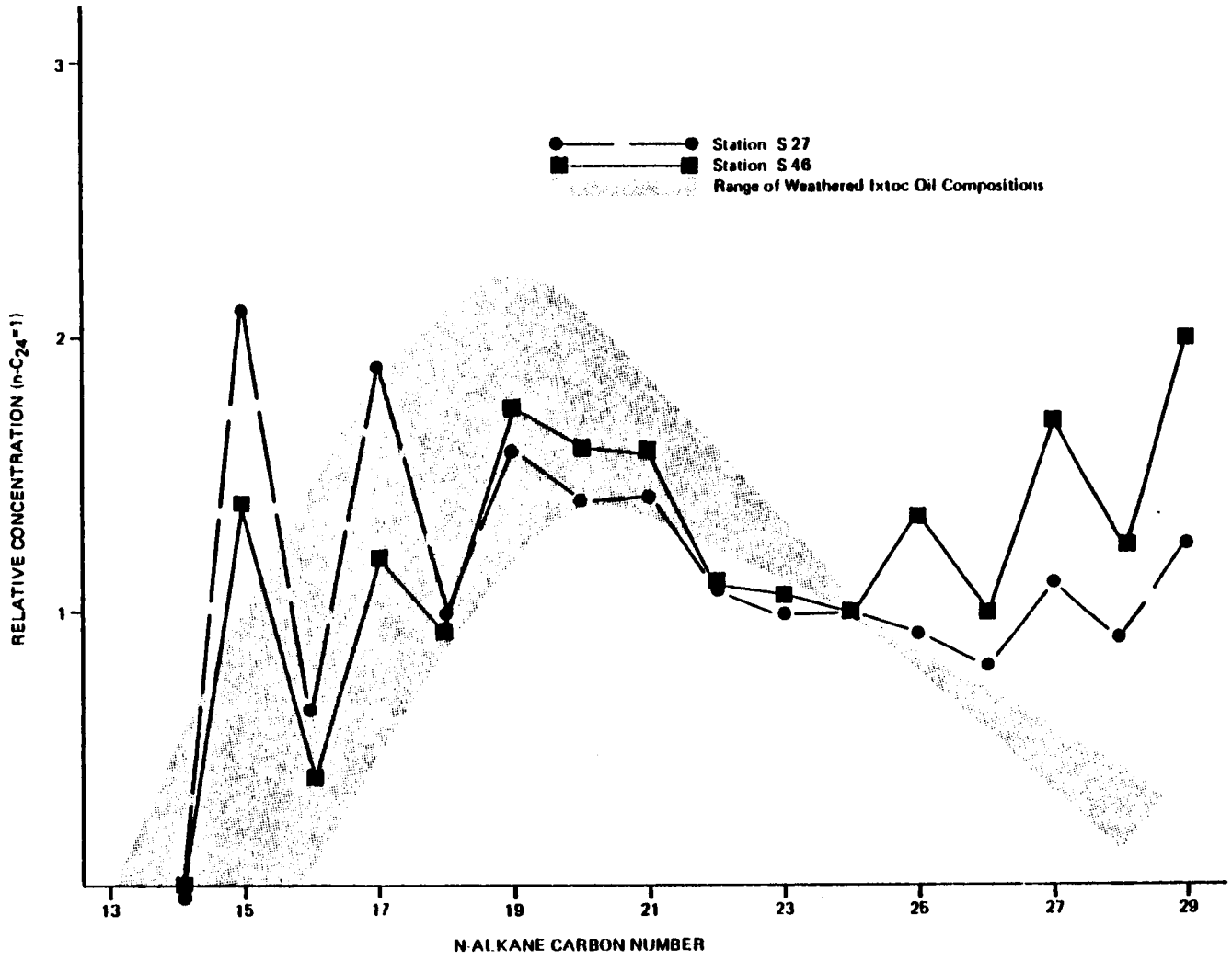


Figure 2–44. Comparisons of n-alkane Composition of Oiled Sorbent Pads with Neat Oils.

This latter experiment proved most revealing. Incremental additions of Ixtoc oil were made to a shrimp extract to examine the qualitative changes in the synchronous UV/F spectra so as to facilitate the detection of Ixtoc oil residues in the tissues and to examine the additivity of this response. These incremental additions are shown in Figure 2-45. While the UV/F response of the two wavelengths monitored (312 and 350 nm) was additive, a substantial 312-nm background was observed. This 312-nm background had been noted before (Boehm and Fiest, 1980c) in shrimp from the Texas-Louisiana coasts, probably owing to a combination of biolipid fluorescence and background PHC levels. Although the additivity is apparent (Table 2-28), the incremental (nonquenched) response becomes roughly linear only at concentrations greater than ∿1.0 ppm. For a 20-μg (∿2 ppm) addition of oil to the observed background, the expected change, based on the sum of the "oil alone" UV/F trace and the "background" trace, was in reasonable agreement (11% @ 312 nm; 48% @ 350 nm) with that actually observed (Table 2-28).

Perhaps the more important part of this experiment was the appearance of the significant and variable 312-nm background. The 350-nm band is not a significant feature of the nonoiled shrimp, making the 350-nm band (and/or the 400-410 band if it appeared) more diagnostic for oil than consideration of the two-ringed (312-nm) band alone (Figure 2-45). The oil addition series reveals the significance of the 350-nm band. Also of importance at higher concentration levels is the nonquenched ratio of 312/350 nm. Background ratios were roughly 5-10 while the ratio in oil was 2. Thus as concentrations of oil increased to the 2-ppm level (Table 2-28) this ratio approaches the oil value. A summary of this ratio in the shrimp samples examined appears in Figure 2-46, which shows that by this criterion many shrimp samples exhibited the potential for recent oil additions. Many of those samples were chosen for additional analytical work by virtue of this ratio value and by virtue of a prominent 350-nm band (e.g., Figure 2-47).

Shrimp "No. 2 fuel oil equivalent" concentrations were calculated based on the 312-nm response in the synchronous mode and for both the 312- and 350-nm bands in the fixed excitation mode. Good agreement was achieved by comparison of synchronous and fixed-excitation quantification although, as previously stated, these values do not represent quantities of "oil" due to considerable 312-nm background.

2.3.4.2 FSCGC Analysis

Forty-six samples were chosen for further (FSCGC) analysis based on the UV/F results outlined above. Giam et al. (1980) have previously discussed the historical Penaeus aztecus data from the STOCS program and have noted seasonal hydrocarbon (n-alkane) compositional variations summarized in Figure 2-48. Based on their evaluation of the historical data, several data treatments seemed most appropriate for consideration in the mid- and post-spill samples, namely: (1) consideration of FSCGC compositional information (n-alkanes) and (2) aromatic hydrocarbon data (see next section 2.3.4.3), (both in view of the composition of the potential source materials).

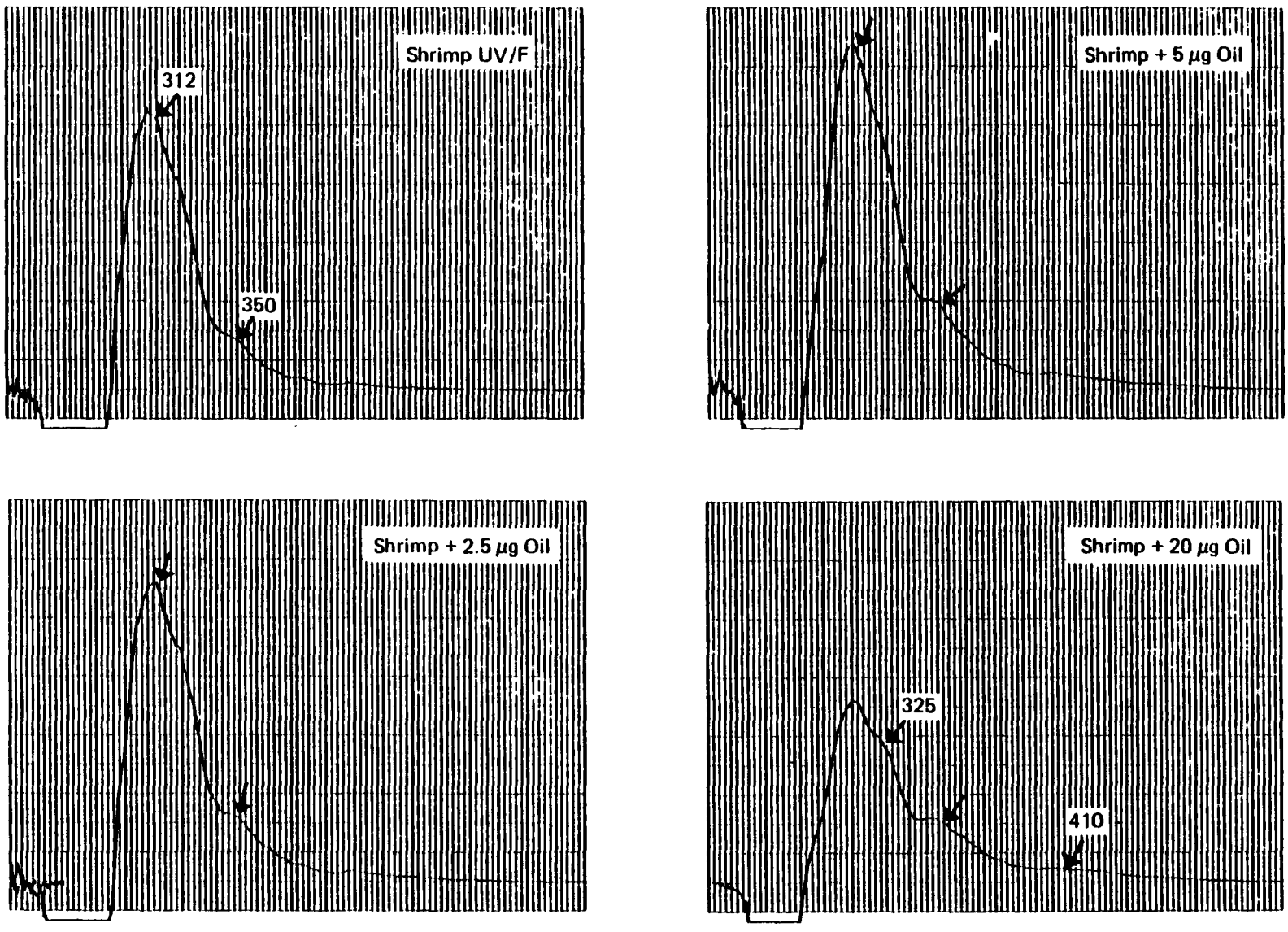


Figure 2–45. Serial Addition of IXTOC Oil to Shrimp Extract.

TABLE 2-28

UV/F RESPONSES TO INCREMENTAL ADDITIONS OF OIL TO A TISSUE EXTRACT

	WAVELENGTH (nm)			OIL ADDED (g)	APPROXIMATE OIL CONCENTRATION ($g \cdot g^{-1}$ dry weight)
	312	350	312/350		
1)	45.5	7.5	6.1	0	0
2)	47.5	8.5	5.9	1.0	0.1
3)	51	11.5	4.4	2.5	0.25
4)	59	15	3.9	5.0	0.5
5)	75	22	3.4	10.0	1.0
6)	103	53	1.9	20.0	2.0
1)	45.5	7.5		Background	
	64.4	28.1		Expected incremental change (20 g addition) (from oil UV/F trace)	
6-1)	57.5	45.5		Observed change	

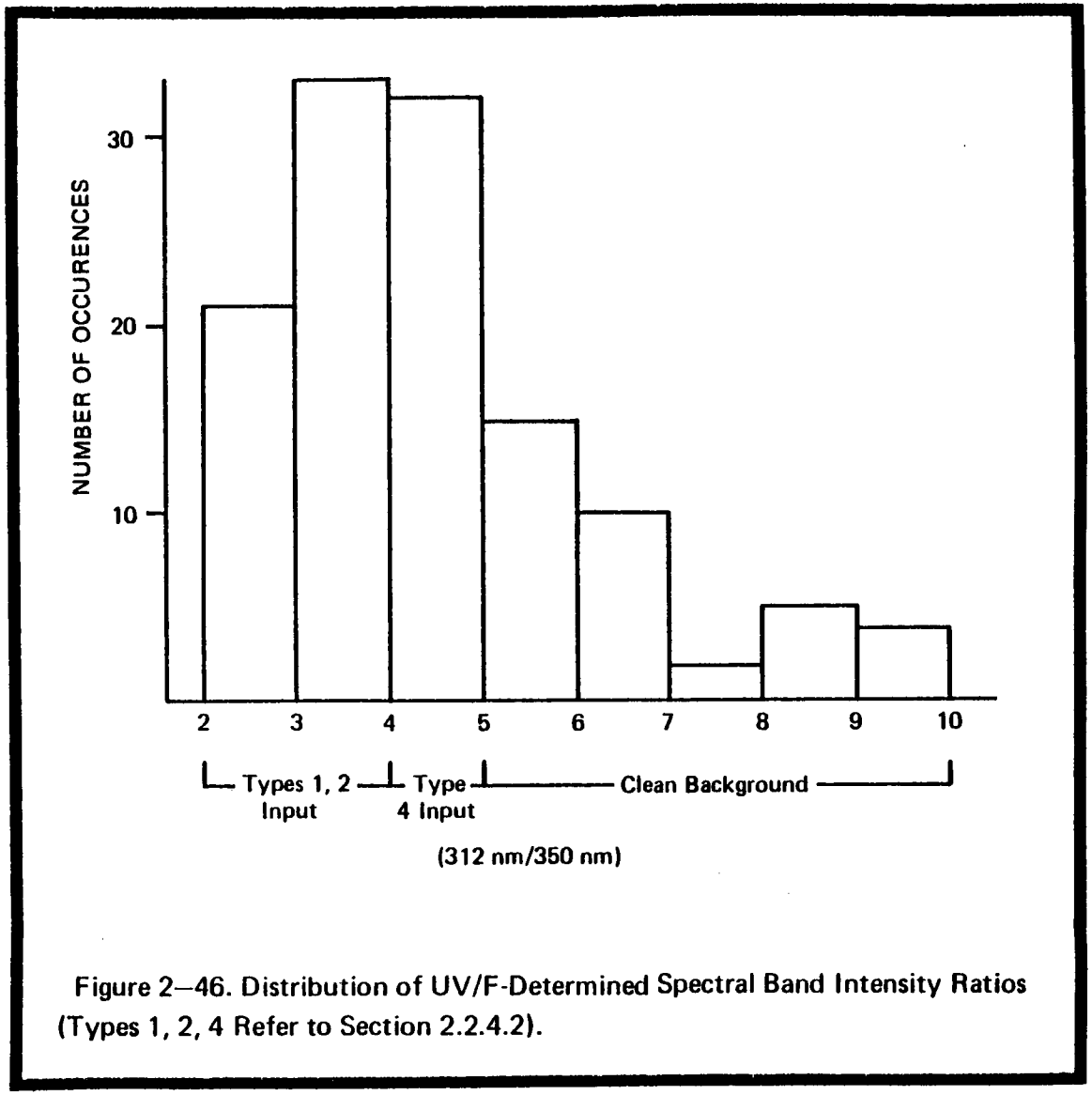


Figure 2—46. Distribution of UV/F-Determined Spectral Band Intensity Ratios (Types 1, 2, 4 Refer to Section 2.2.4.2).

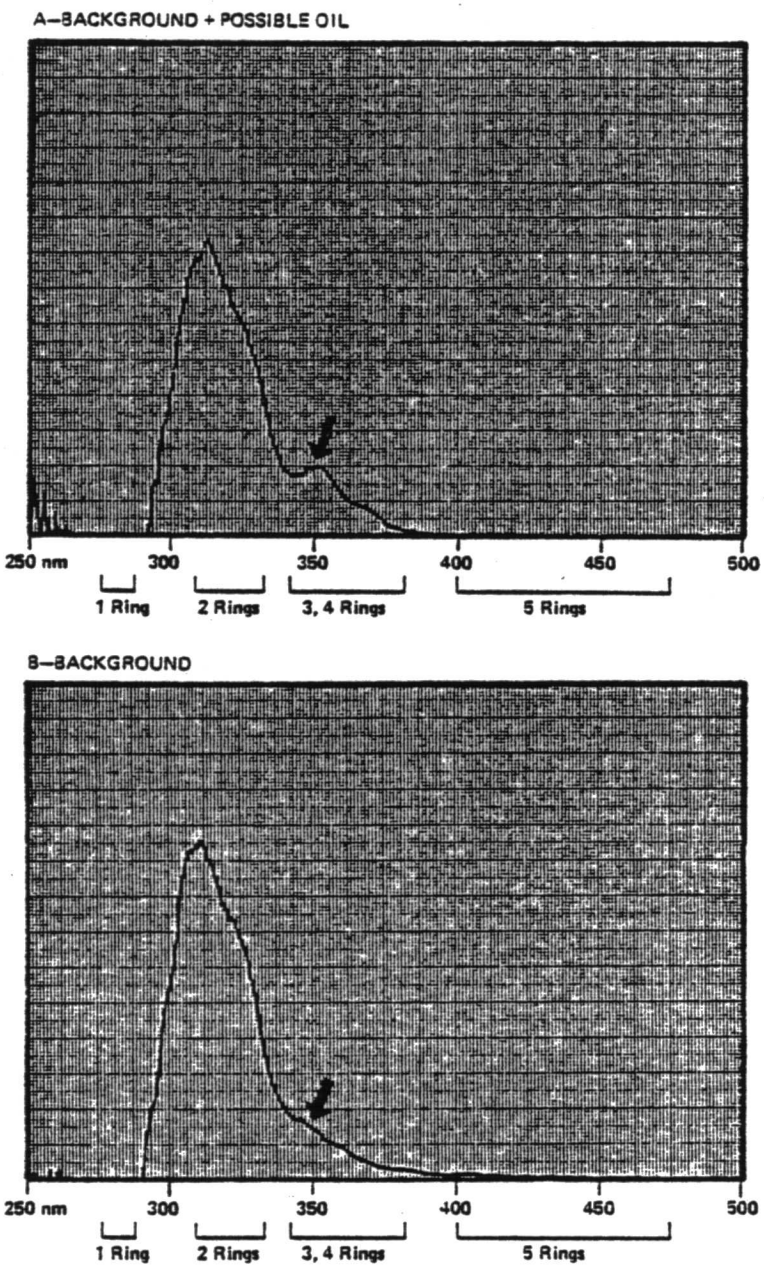


Figure 2—47. Representative Synchronous UV/F Spectra of Shrimp.

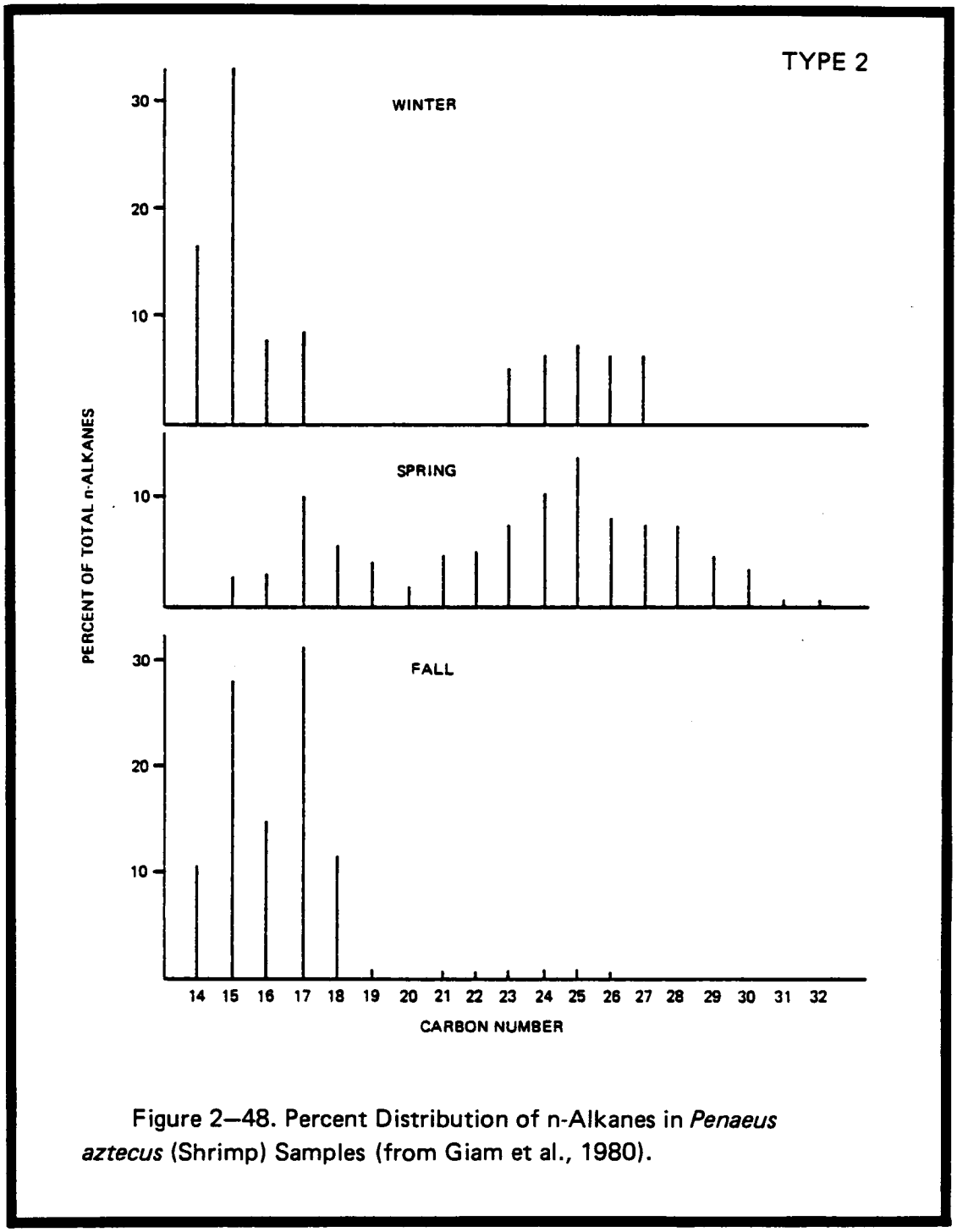


Figure 2—48. Percent Distribution of n-Alkanes in *Penaeus aztecus* (Shrimp) Samples (from Giam et al., 1980).

Parameters involving alkanes and alkane/isoprenoid relationships were considered to be inappropriate as diagnostic tools due to both the considerable biogenic hydrocarbon inputs to the shrimp (e.g., pristane, n-C_{17}, n-C_{15}) as well as the differential uptake of oil by marine organisms (Neff et al., 1976; Boehm et al., 1982) and pre-uptake weathering that one expects in this type of spill. Nevertheless if one compares the historical data on saturated hydrocarbons with mid- and post-spill data (Table 2-29), some differences in the parameter means are revealed. However, due to the wide variability in these data and due to the fact that almost none of the alkane variability can be ascribed to petroleum additions, we view this comparison of saturated hydrocarbon parameters to be inappropriate for this assessment study.

Four distinctly different compositional patterns were observed (Figures 2-48 and 2-49) based on the saturated hydrocarbon composition. A summary of the total hydrocarbon data, by FSCGC type, appears in Table 2-30. Detailed data appear in Appendix 9.1. Type 1 (Figure 2-50) is characteristic of a fresh oil and was found in one sample from 1979 (Sector W07, July 1979, in the northern part of the study area). This sample predates the observable movement of Ixtoc oil into the study area. The n-alkane pattern does not match Ixtoc oil nor does the aromatic hydrocarbon data (see next section). Several Type 2 samples associated with weathered oil (Figure 2-51) were found in 1979 from sector W06 (August and November 1979) and from sector W05 (December 1979). These residues, which are characterized by a prominent mid-boiling UCM and an overriding series of branched/isoprenoid hydrocarbons, are characteristic of assimilated petroleum residues subjected to weathering and differential uptake (Boehm et al., 1982). No definitive source can be associated with these residues from FSCGC data. Chromatogram types 3 and 4 are similar to those observed by Giam et al. (1980) (see Figure 2-49). Type 3 is characterized by a prominent series of high molecular weight n-alkanes usually without a significant underlying UCM. This distribution is commonly encountered in coastal animal populations (Boehm, 1980) and although its precise source is not known (though believed to be related to microbial activity), it is not petroleum-related. A similar pattern was ascribed to a seasonal dietary influence (Spring) by Giam et al. (1980).

Type 4 distributions have been observed by Giam et al. (1980) in winter samples from the STOCS area. It includes samples having bimodal n-alkane distributions usually over a minor-to-moderate bimodal UCM, with or without a slight odd-carbon predominance in the n-C_{25} to n-C_{33} region (i.e., of sedimentary origin). These samples are influenced by a chronic petroleum input or inputs, but are not related to any recent oil spills.

Most of the recent petroleum inputs seen in the samples result in PHC concentrations between 15 and 40 ppm compared with background values from 0.2 to 8 ppm. The incidence of recent PHC additions, including fresh and weathered oils, is confined to the northern part of the study area (sectors W05 [n=1], W06 [n=3], and W07 [n=1] in 1979, and sectors W07 [n=2], X10 [n=1], Z03 [n=1], and Y04 [n=1] in 1980). Note that the W sectors (Figure 2-6) are well outside of the STOCS study area (X03,04; Y03,04, Z03,04). Thus the W sectors and X10 sector could very well have been influenced by other

TABLE 2-29

COMPARISON OF SATURATED HYDROCARBON PARAMETERS IN PENAEID SHRIMP SAMPLES (Penaeus aztecus)

		TOTAL ALKANES (µg/l)	SUM OF ALKANES (%)			PRISTANE / PHYTANE	PRISTANE / C_{17}	PHYTANE / C_{18}	CPI_{14-20}	CPI_{20-32}
			C_{14} - C_{18}	C_{19} - C_{24}	C_{25} - C_{32}					
1975-1977	STOCS	0.14±0.28 (48)	39.7±7.2 (34)	9.1±12.7 (34)	51.1±39.1 (34)	44.0±58.0 (2)	2.0±1.7 (17)	0.2±0.1 (2)	1.6±0.6 (5)	6.8±10.1 (22)
Damage Assessment	1979	1.09±2.62 (15)	34.46±22.21 (15)	23.76±19.49 (15)	39.78±23.01 (15)	4.15±2.26 (11)	1.25±0.89 (15)	0.38±0.39 (15)	1.27±0.72 (15)	1.57±0.48 (15)
	1980	0.86±1.51 (17)	29.8±19.9 (17)	41.3±79.0 (17)	28.9±17.7 (17)	4.06±2.26 (9)	0.76±0.49 (16)	0.23±0.32 (16)	1.36±0.56 (17)	2.67±3.14 (17)

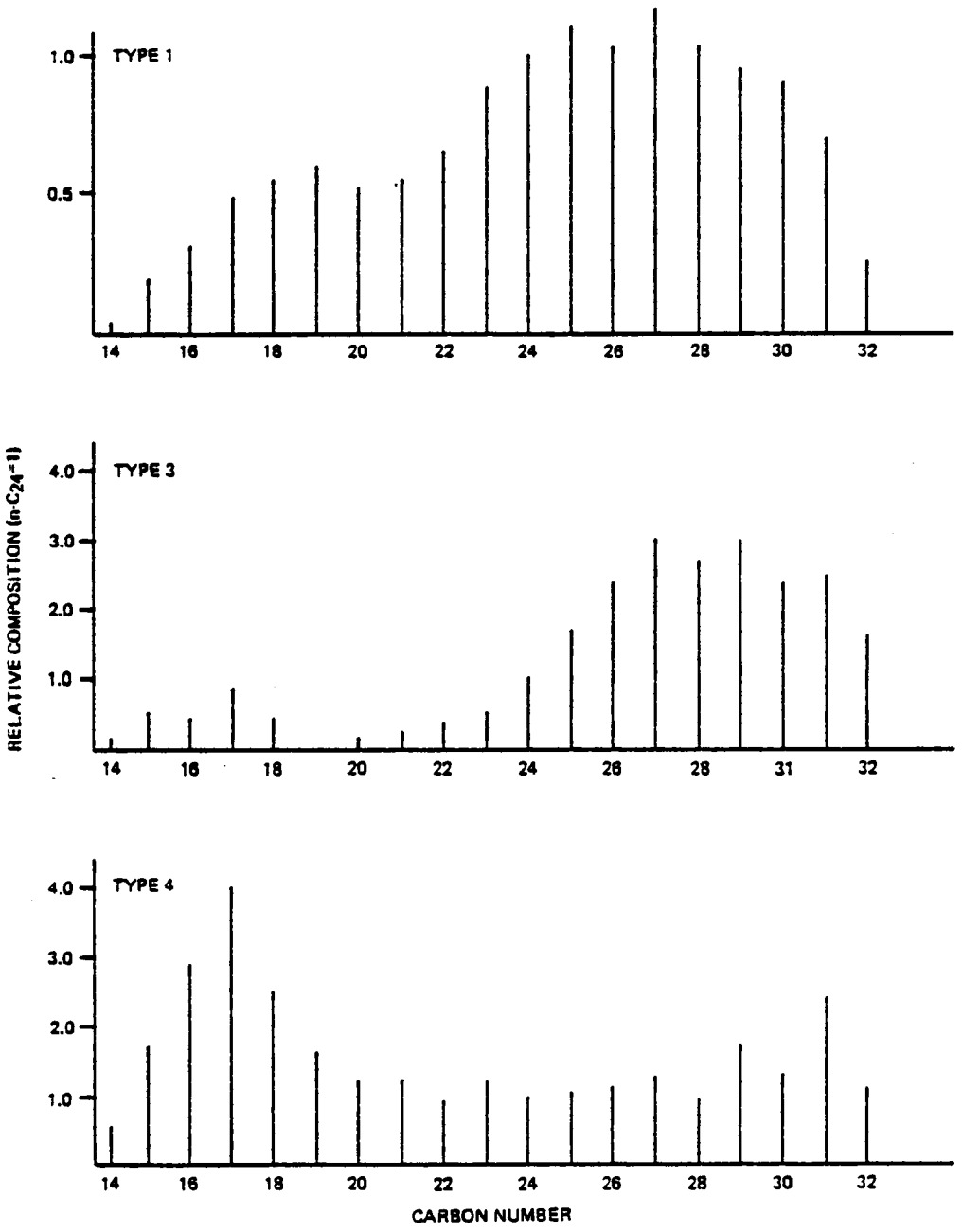


Figure 2—49. Typical n-Alkane Compositional Profiles of Shrimp from the Study Region.

TABLE 2-30

SUMMARY OF QUANTITATIVE PENAEUS AZTECUS DATA BY FSCGC TYPE
($\mu g \cdot g^{-1}$)

COMPOSITIONAL TYPE[a]	YEAR	
	1979	1980
1	37 (n=1)	none
2	16.1 ± 5.1 (n=5)	20.9 ± 8.7 (n=4)
3	5.9 ± 1.6 (n=4)	7.5 ± 5.5 (n=4)
4	4.4 ± 2.0 (n=6)	2.0 ± 0.9 (n=14)
5 (clean)	2.2 ± 1.3 (n=4)	2.0 ± 1.3 (n=4)

[a]Type refers to Figure 2-49.

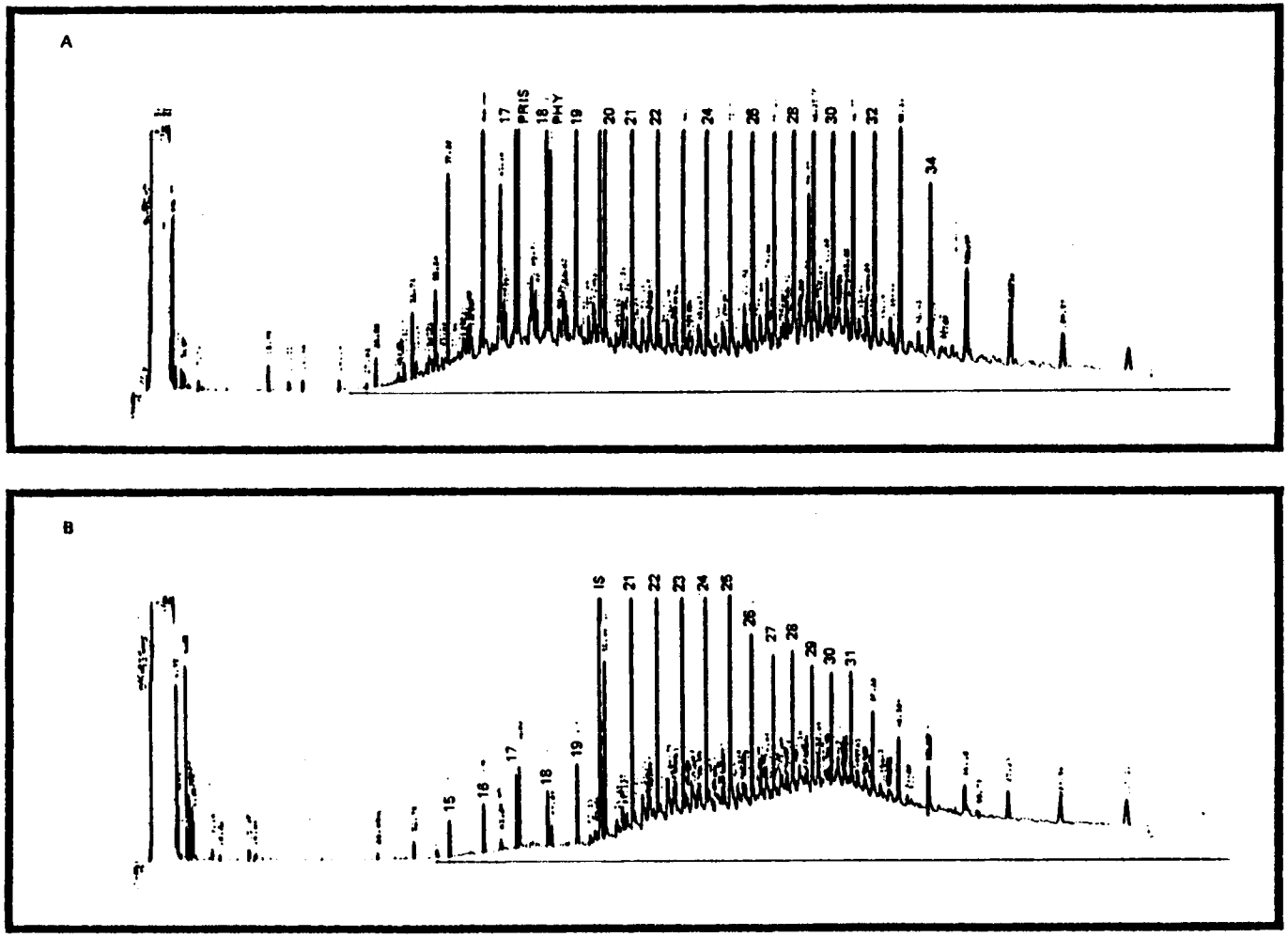


Figure 2–50. Type I FSCGC Saturated Hydrocarbon Traces (Oil) of Shrimp Samples (A–Station W–07; August 1979, B–Station S–15; December 1980).

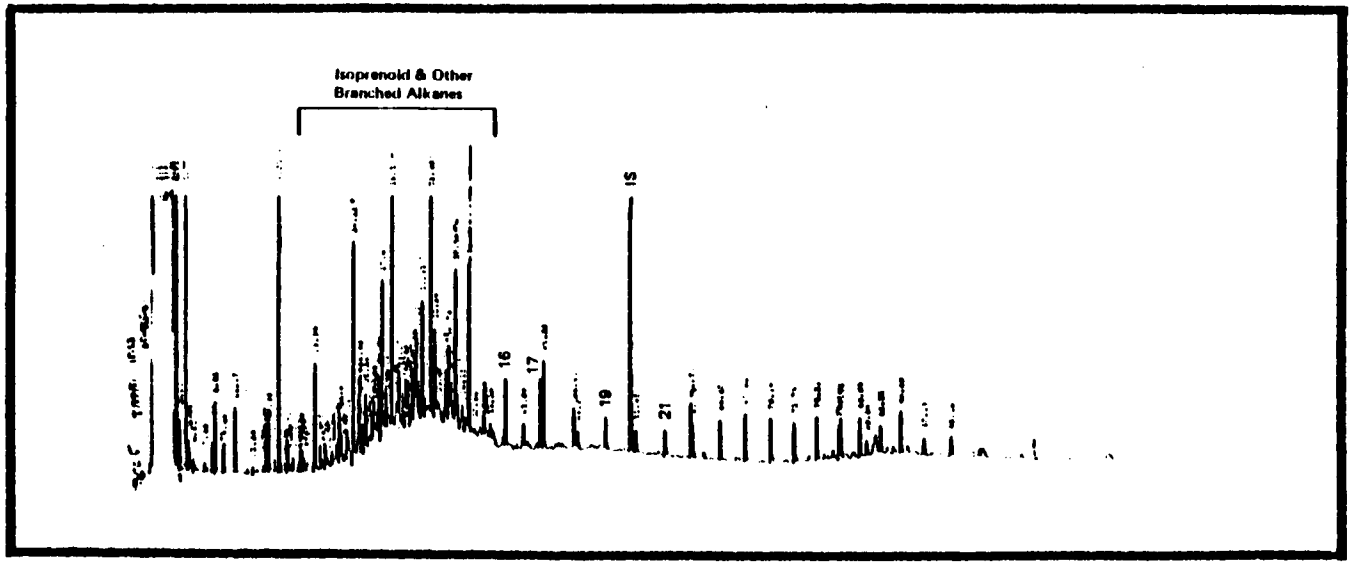


Figure 2–51. Type 2 FSCGC Saturated Hydrocarbon Pattern (Weathered Oil) in Shrimp.

inputs to the region, including industrial activities near Galveston and the Mississippi River inputs, as well as a myriad of point sources (e.g., drill rigs, tanker discharges, etc.). As will be demonstrated in the next section, only one of the aromatic hydrocarbon residue assemblages can be ascribed to Ixtoc spill input and not to Burmah Agate oil.

Additionally, if only the samples from the STOCS region are considered, most (15 of 20 = 75%) of the 1980 samples analyzed by FSCGC fall into Type 4 composition, as do nearly all (6 of 7 = 86%) of the 1979 FSCGC samples. Thus the Giam et al. (1980) winter GC-type (Figure 2-48) was the predominant FSCGC type observed here. However, Giam et al. (1980) report little if any UCM material, while many of the 1979 and 1980 Type 4 samples contained unimodal or bimodal UCM. We believe these UCM distributions are chronic additions to the biota rather than spill related, as we have seen these UCM distributions in tissues from the Western Gulf previously (Boehm and Fiest, 1980c). PAH compounds (see next section) accompany these chronic pollutant UCMs and account for many of the UV/F 312/350 ratios in the 4 to 5 aromatic ring range previously noted.

2.3.4.3 Aromatic Hydrocarbons in Shrimp by GC/MS

To assess the impact of the Ixtoc I incident on the Texas Gulf Coast marine ecosystem, the aromatic hydrocarbon content of seventeen shrimp samples was determined by GC/MS. Although aromatic hydrocarbons are known chemical carcinogens, their effects on marine ecosystems are presently unknown (King, 1977). Hence, any data pertaining to the aromatic content of marine organisms exposed to a petroleum contaminated environment are of importance. The petrogenic (Group I) aromatic and pyrogenic PAH (Group II) content of the shrimp analyzed in this study is presented in Appendix 9.1 and summarized in Table 2-31.

Most samples contained only minimal amounts of four- and five-ringed aromatic compounds (pyrogenic PAH). Fluoranthene and pyrene were the only prevalent aromatics, usually present at concentrations of 1 to 5 $ng \cdot g^{-1}$. In only two samples (one at Station W05 and one at Station W06) were all the Group II aromatics present.

The petrogenic aromatic content of shrimp was used to determine whether petroleum hydrocarbons had been incorporated into this part of the Texas OCS ecosystem. In particular, alkyl phenanthrene-alkyl dibenzothiophene ratios were again examined to define the level of contamination and a possible source, as was done for sediments (see Section 2.3.3.3). Using this criterion, eleven of seventeen shrimp samples were found to have significant quantities of petrogenic aromatics which would suggest petroleum hydrocarbon uptake. A summary of the alkylated phenanthrene-dibenzothiophene ratios is presented in Table 2-31. The ratios for the Ixtoc I oil and Burmah Agate oil are presented elsewhere (see Section 2.3.1.3). In only one shrimp sample do the ratios compare favorably to those of the Ixtoc I oil (Station W06, September 1970). For all other samples the ratios, although generally similar to each other,

TABLE 2-31

ALKYL PHENANTHRENE-ALKYL DIBENZOTHIOPHENE RATIOS IN SHRIMP SAMPLES

STATION	DATE	TOTAL AROMATICS ($ng \cdot g^{-1}$) GROUP 1	GROUP 2	C_1P/C_1DBT	C_1P/C_2DBT	C_3P/C_3DBT
W05	DEC. 1979	380	55	3.15	2.86	5.78
W06	AUG. 1979	70	2	not enough aromatics present to calculate		
W06	SEPT. 1979	110	7	1.18	0.48	0.34
W06	NOV. 1979	710	55	3.00	3.03	4.51
W06	NOV. 1979	200	6	3.95	—	--
W07	SEPT. 1979	220	14	3.02	2.91	4.68
W07	OCT. 1979	450	2	3.12	3.06	2.00
W07	JAN. 1980	10	2	not enough aromatics present to calculate		
Y04	OCT. 1979	120	9	4.06	3.00	1.88
Y04	NOV. 1979	130	8	not enough aromatics present to calculate		
X07	SEPT. 1979	10	ND	not enough aromatics present to calculate		
G03	DEC. 1980	20	2	not enough aromatics present to calculate		
S46	DEC. 1980	50	3	7.64	5.11	--
M04	DEC. 1980	10	1	not enough aromatics present to calculate		
M05	DEC. 1980	20	1	4.33	1.50	--
M24	DEC. 1980	50	5	6.10	2.43	1.33
M36	DEC. 1980	50	5	6.25	2.17	2.67

are quite different than either the Ixtoc I or Burmah Agate ratios. This may be explained as being the result of preferential uptake of certain aromatics, preferential metabolism of certain aromatics, or uptake of petroleum from an unknown source. Petrogenic aromatics are in the shrimp tissues prior to either spill impact (Station W06, August 1979) and the elevated P/DBT ratios are characteristic of the shrimp prior to the Burmah Agate spill.

The petrogenic aromatics are far more abundant in the shrimp than the pyrogenic PAH, thus completely decoupling the shrimp from the surface sediment hydrocarbon composition, but perhaps not from the petroleum-aromatic-rich material found in the water column in the sorbent pad samples.

2.3.5 Quality Control Program

To ensure the quality of data generated during an analytical program of this type, two forms of quality control were employed: internal and external. The former involves: (1) monitoring the levels of the compounds of concern (PHC and PAH) in procedural blanks; (2) the daily calibration of instruments, calculation of response factors, and monitoring of column performance; and (3) routine analysis of sample splits (duplicates). The results of these duplicate analyses are presented in Tables 2-32 and 2-33. Additionally, "blind" spiked samples (PAH) were analyzed by the GC/MS facility periodically during this study and results always fell within $\pm$12 percent of actual value.

This program was unique in that the successful completion of five major "external" quality control elements were required prior to and during the program. Three intercalibration exercises using actual environmental samples (one performed in duplicate) and an on-site working evaluation were undertaken. The pertinent results of the Duwamish II sediment, the Texas IRM, and the EPA Megamussel (twice during the program) are shown in Tables 2-34, 2-35, and 2-36. The first successful analysis of the Duwamish II sediment sample for a complex array of PAH and alkane components was accomplished by ERCO under this contract. The source of the discrepancies in the Texas IRM sample are not known, although sample heterogeneity as well as errors in either of the two participating laboratories are possibilities. The other results show excellent agreement between the two participating laboratories (NOAA/NAF and ERCO) and with other premier laboratories, and are better than previously accomplished in other published studies (e.g., MacLeod et al., 1981; Hilpert et al., 1978; Wise et al., 1980; Farrington, 1978).

Additionally, a team of analytical chemists from J&W Scientific and NOAA/NAF were dispatched to ERCO to evaluate our performance and to exchange information. The results of this visit plus those of the intercalibration exercises indicated that "state-of-the-art" analyses were being employed successfully in this program (Calder, 1981).

TABLE 2-32

PRECISION OF SATURATED HYDROCARBON MEASUREMENTS

Compound (Parameter) ($\mu g \cdot g^{-1}$)	STATION G03			STATION M26			STATION S04		
	1	2	3	1	2	3	1	2	3
Total alkanes	0.26	0.37	0.36	0.01	0.02	0.03	1.5	1.2	0.9
Sum low	0.01	0.01	0.01	0.003	0.003	0.006	0.003	0.002	0.001
Sum mid	0.06	0.05	0.03	0.002	0.006	0.003	0.14	0.18	0.10
Sum high	0.19	0.31	0.32	0.005	0.011	0.016	1.4	1.0	0.8
n-C_{17}	0.005	0.004	0.005	0.001	0.001	0.001	0.003	0.008	nd
Pristane	0.005	0.004	0.004	nd	nd	nd	nd	0.003	nd
n-C_{29}	0.031	0.035	0.033	0.001	0.001	0.002	0.11	0.16	0.12
n-C_{29}	0.039	0.092	0.087	0.002	0.003	0.004	0.17	0.24	0.23
Total hydrocarbons	6.9	9.4	9.4	1.1 0	0.28	0.75	10.4	15.0	13.6

TABLE 2-33

PRECISION OF AROMATIC HYDROCARBON MEASUREMENTS (STATION S04)

COMPOUND	CONCENTRATION ($ng \cdot g^{-1}$)	
	Rep 1	Rep 2
Naphthalene	ND	1.1
2-methyl naphthalene	ND	0.4
1-methyl naphthalene	ND	0.1
Phenanthrene	2.4	2.8
Methyl phenanthrene	5.2	6.3
Dimethyl naphthalene	3.3	5.8
Fluoranthene	9.5	12.2
Pyrene	16.1	18.5
Benzanthracene	5.6	7.2
Chrysene	8.6	7.8
Benzofluoranthene	28.1	21.9
Benzo(e)pyrene	10.9	9.1
Benzo(a)pyrene	8.4	6.4
Perylene	37.1	31.1

Table 2-34 Mean concentrations ($\bar{x}$) of selected compounds (ng/g, dry wt) ± standard deviations (s) from triplicate analyses of Duwamish II subtidal sediment. Method: 1=tumbler, 2=shaker; solvent: d=dichloromethane, m=methanol.

Laboratory:	NAF_1	NAF_2	ERCO		NAF_1	NAF_2	ERCO
Method, solvent:	1dm	1dm	2dm		1dm	1dm	2dm
Arene	$\bar{x}$±s	$\bar{x}$±s	$\bar{x}$±s	Alkane	$\bar{x}$±s	$\bar{x}$±s	$\bar{x}$±s
Naphthalene	62±4	68±4	43±22	n-C_{14}	130±21	160±15	100±13
2-Methylnaphthalene	48±7	56±4	56±23	n-C_{15}	160±49	230±5	150±27
1-Methylnaphthalene	19±3	19±4	22±8	n-C_{16}	180±32	250±10	140±3
Biphenyl	7.2±0.6	12±2	12±2	n-C_{17}	290±81	400±6	200±45
2,6-Dimethylnaphthalene	41±3	45±6	40±3	Pristane	440±150	600±17	490±140
2,3,5-Trimethylnaphthalene	33±11	23±10	29±6	n-C_{18}	190±49	250±6	170±35
Fluorene	110±6	110±10	110±20	Phytane	290±76	440±17	260±64
Dibenzothiophene	75±1.5	78±7	91±8	n-C_{19}	220±56	190±6	170±30
Phenanthrene	650±32	700±30	900±36	n-C_{20}	150±64	210±25	230±31
Anthracene	260±21	280±38	300±81	n-C_{21}	420±100	590±10	230±44
1-Methylphenanthrene	100±18	99±2	50±11	n-C_{22}	150±64	220±15	150±27
Fluoranthene	1500±120	1800±120	2000±300	n-C_{23}	290±110	320±35	270±77
Pyrene	1300±58	1400±58	1800±170	n-C_{24}	240±12	200±31	180±62
Benz[a]anthracene	560±25	590±23	1300±400	n-C_{25}	480±140	570±97	510±74
Chrysene	1000±58	1000±58	950±170	n-C_{26}	240±56	180±45	230±77
Benzo[e]pyrene	560±36	560±35	710±270	n-C_{27}	700±200	830±67	790±81
Benzo[a]pyrene	620±36	640±26	610±130	n-C_{28}	190±91	210±78	530±130
Perylene	270±20	270±17	500±300	n-C_{29}	1300±100	1100±58	1800±170
				n-C_{30}	180±55	160±42	240±71
				n-C_{31}	1500±380	1500±120	1900±470

Table 2-35 Mean concentrations ($\bar{x}$) of selected hydrocarbons (ng/g, dry wt) ± standard deviations (s) from triplicate analyses of Texas IRM sediment. Method: 1 = tumbler, 2 = shaker; solvent: d = dichloromethane, m = methanol; (--) = compound not determined.

Laboratory:	NAF_1	NAF_2	ERCO		NAF_1	NAF_2	ERCO
Method, solvent:	1dm	1dm	2dm		1dm	1dm	2dm
Arene	$\bar{x}\pm s$	$\bar{x}\pm s$	$\bar{x}\pm s$	Alkane	$\bar{x}\pm s$	$\bar{x}\pm s$	$\bar{x}\pm s$
Naphthalene	2.7±0.06	2.6±0.3	0.2±0.2	n-C_{14}	1.6±0.2	1.6±0.4	--
2-Methylnaphthalene	1.8±0.2	1.6±0.3	1.3±0.4	n-C_{15}	5.0±0.2	4.9±1.0	--
1-Methylnaphthalene	1.1±0.1	1.0±0.2	0.5±0.1	n-C_{16}	2.6±0.4	2.6±0.5	1±0.7
Biphenyl	<0.23	<0.23	0.4±0.3	n-C_{17}	9.8±0.2	9.7±1.4	7±1.0
2,6-Dimethylnaphthalene	<0.23	<0.23	0.9±0.2	Pristane	5.9±0.6	5.9±0.8	3±0.6
2,3,5-Trimethylnaphthalene	<0.24	<0.24	0.6±0.2	n-C_{18}	3.2±0.3	3.1±0.5	19±2.6
Fluorene	<0.24	<0.24	0.8±0.2	Phytane	1 6±0.6	17±2.0	2±0
Dibenzothiophene	<0.27	<0.27	1.0±0.5	n-C_{19}	7.1±1.2	6.9±0.7	11±0.6
Phenanthrene	2.5±0.4	2.1±0.6	9.1±3.5	n-C_{20}	3.8±0.4	3.6±0.4	5±0.6
Anthracene	<0.19	<0.19	1.3±0.7	n-C_{21}	37±0.6	36±6.4	2±0.6
1-Methylphenanthrene	<0.29	<0.29	1.5±0.5	n-C_{22}	6.3±0.4	6.3±0.9	7±3.5
Fluoranthene	5.4±1.1	4.5±0.7	17±8.9	n-C_{23}	13±0.6	14±2.3	10±1.5
Pyrene	8.4±1.0	7.2±1.6	18±9.1	n-C_{24}	7.8±0.5	7.6±12	7±0.6
Benz[a]anthracene	1.8±0.7	2.0±1.1	8.4±4.9	n-C_{25}	20±1.0	20±4.2	19±3.5
Chrysene	3.6±1.0	2.9±2.2	11±4.8	n-C_{26}	10±0.6	9.7±1.4	11±4.5
Benzo[e]pyrene	4.1±0.4	4.8±2.8	11±3.5	n-C_{27}	46±3.8	42±13	34±6.1
Benzo[a]pyrene	2.2±0.2	2.7±1.6	8.5±3.7	n-C_{28}	14±1.0	14±2.5	11±2.6
Perylene	1.5±0.1	1.7±0.5	32±5.7	n-C_{29}	78±7.5	71±18	98±16
				n-C_{30}	19±5.3	19±6.7	14±1.5
				n-C_{31}	110±12	92±27	60±12

TABLE 2-36

MEAN CONCENTRATIONS ($\bar{x}$) OF SELECTED HYDROCARBONS ± STANDARD DEVIATIONS (s) IN EPA MUSSEL HOMOGENATE

(Concentration: $ng \cdot g^{-1}$ dry wt)

LABORATORY:	NAF	$ERCO_1$	$ERCO_2$	ERL/N	UNO	WHOI
	(n=10)	(n=3)	(n=2)			
HYDROCARBON	$\bar{x} \pm s$	$\bar{x} \pm s$	$\bar{x} \pm s$	$\bar{x} \pm s$	$\bar{x} \pm s$	$\bar{x} \pm s$
$n\text{-}C_{14}$	23 ± 5	25 ± 9	--	--	--	--
$n\text{-}C_{15}$	205 ± 17	91 ± 7	--	--	--	--
$n\text{-}C_{16}$	32 ± 6	51 ± 6	--	--	--	--
$n\text{-}C_{17}$	195 ± 25	109 ± 8	--	--	--	--
Fluoranthene	62 ± 11	140 ± 12	89 ± 4	56 ± 18	42 ± 37	80 ± 12
Pyrene	36 ± 8	120 ± 12	74 ± 4	46 ± 13	34 ± 31	92 ± 14

n = number of replicates
(--) = no data submitted

2.4 Discussion

Identifiable residues of oil from the Ixtoc I blowout were observed on the South Texas barrier beaches through December 1980 (this study), and were redeposited on offshore tar reefs within several hundred metres from shore (Tunnell et al., 1981). The offshore movement and sedimentation of these deposits and/or the direct deposition of weathered Ixtoc petroleum were, prior to this study, of unknown magnitude and importance.

Two comprehensive benthic sediment sampling programs and the subsequent fine-tuned analytical program established in this study to look for recent petroleum residues have failed to detect any definitive traces of Ixtoc oil in the benthic substrate. Therefore no offshore benthic impact from this spill event can be postulated for the observed biological perturbations (see Section 4). Identifiable residues of Burmah Agate oil were detected in the "G" sediment series near the collision site off Galveston, well to the north of the STOCS study area. These residues appear to be confined to the region (within $\sim$30 km) of the wreck. The Port Aransas Channel sediments did contain petroleum residues ($\sim$10 ppm), possibly of an Ixtoc origin.

The lack of observable Ixtoc I or Burmah Agate oil input to the offshore sediments may be attributed to one or a combination of several factors:

1. These petroleum residues may reside in the uppermost sediment layers, that is the mobile floc, and thus are both mobile and difficult to sample with most conventional techniques (e.g., Smith MacIntyre grab).

2. Most of the beached oil may reside in inshore regions not sampled in this study or may reside in extremely patchy distributions.

3. Levels of sediment-bound oil may be very low (ppb) due to the oils distribution over a wide region and thus is not detectable in depositional areas (fine-grained sediments) having relatively high hydrocarbon background levels (5-20 ppm).

4. Suspended sediment values in the region are very low outside of nepheloid layers and hence a sorbing surface for oil in the water was not readily available slowing the oils transport to the sediment.

Thus for the most part the examination of the sediment grab samples was a geochemical update of the STOCS baseline studies with several very significant refinements. The offshore benthic environment, previously characterized as a near-pristine environment, was shown to be significantly impacted by polynuclear aromatic hydrocarbon residues, probably of anthropogenic origin. High-resolution capillary gas chromatography and gas chromatographic mass spectrometry have revealed a widespread abundance of PAH compounds (1-100 ppb), part of the 1-20 ppm total hydrocarbon levels. The PAH distributions suggest areawide, non-point source distributions largely determined by normal geochemical transport and sedimentation patterns, with absolute quantities co-varying with total organic carbon content of the sediment.

Such offshore PAH residues are not uncommon (Overton and Laseter, 1980; Bieri et al., 1978; Boehm, 1978) in OCS sediments. PAHs are ubiquitous chemical constituents throughout the geosphere (Youngblood and Blumer, 1975; Laflamme and Hites, 1978), having been detected in marine sediments (Laflamme and Hites, 1978; Windsor and Hites, 1979; Prahl and Carpenter, 1979; Lake et al., 1979; Hites et al., 1980), lake sediments (Muller et al., 1977; Wakeham et al., 1980a), various soils (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Blumer et al., 1977), airborne particulate matter (Daisey and Leyko, 1979; Bjorseth et al., 1979; Handa et al., 1980; Cloudhury and Bush, 1981; Yu and Hites, 1981), natural waters (Herbes, 1977), and even drinking water (Basu and Saxena, 1978; Sorrell et al., 1980).

Many sources are considered possible contributors to global distributions of PAH. The most likely sources are natural and anthropogenic combustion. A combustion source is consistent with the fact that throughout the world the qualitative distributions of PAH are remarkably similar and the quantitative abundances increase with proximity to urban regions (Laflamme and Hites, 1978). For example, Davies et al. (1976) found substantial quantities of PAH with a distribution similar to those cited by Laflamme and Hites (1978) in the combustion effluent of municipal refuse. Lee et al. (1977) noted that the PAH produced from the combustion of kerosene correlated closely with certain molecular weight regions of the PAH found in Charles River sediments. Natural combustion products originate from forest and prairie fires (Laflamme and Hites, 1978). Other sources which may contribute PAH burdens to the environment include spill-related petroleum hydrocarbon contamination, which is of particular interest in this study, natural petroleum seepage (Reed and Kaplan, 1977; Levy and Ehrhardt, 1981), and *in situ* chemical aromatization of naturally occurring cyclic compounds (e.g., Frenkel and Heller-Kallai, 1977; Schaefle et al., 1978; Wakeham et al., 1979).

There is some pressing evidence that *Ixtoc* oil was, at least during the mid-spill period (1979), present in the near-shore suspended sedimentary system either as part of nepheloid layers or as part of a remobilized and difficultly sampled mobile flocculent layer. *Ixtoc* oil residues (200-500 ppm) were definitely identified in sorbent pad samples obtained from near-shore oblique (bottom-to-surface) plankton tows. The non-visible oil was apparently tied up in sediment material rather than present as visible tar balls. While there is no direct evidence for linking these residues to the benthic substrate on which the benthic fauna dwells and feeds, and hence to any impact or "damage," several previous studies point to the possibility that deficiencies in sampling techniques could have resulted in false negative results. Both laboratory studies (Wade and Quinn, 1980; Gearing et al., 1980) and field investigations (Boehm et al., 1982) have indicated that newly deposited oil is difficultly sampled due to the propensity for conventional samplers to "blow away" the top several millimeters of sediment (i.e., the most recently deposited material) upon sampler impact. The sorbent pad data definitively indicate only that *Ixtoc* oil residues were in the particulate water column material and neither directly links these residues with sedimentary concentrations nor signifies a possible biological impact.

A thorough examination of the levels and source(s) of petroleum hydrocarbons in penaeid shrimp tissues taken during and after the spill from a variety of sampling locations, has revealed widespread low-level petroleum contamination in this commercially important resource, but not related to the Ixtoc or other known spills. Nonidentifiable, but readily detected oil contamination was seen in several samples in the low-ppm range at stations within and outside of the study area (STOCS). Note that, as determined in this study, shrimp collected in the Galveston-to-Mississippi delta offshore region contain greater amounts of petrogenic residues than do the STOCS shrimp samples (Giam et al., 1980). Previous STOCS data (Giam et al., 1980) had indicated little if any petroleum contamination in the region, and our data are not consistent with these findings, presumably due primarily to refinements of analytical techniques employed. Fresh and weathered petroleum residues, many of which were observed in samples taken well to the north of the study region, could not be related to a specific source (i.e., Ixtoc or Burmah Agate). Some of the many possible oil discharge sources in the region probably account for these observations. Giam et al. (1980) did not report petroleum residues in shrimp samples similar to those representing type 1 and 2 residues (see Figures 2-50, 2-51). The sporadic occurrence of petroleum residues observed here represents a new finding, although one should expect to find such levels (5-20 ppm) of petrogenic residues in an area chronically impacted with tar and other petroleum materials (Boehm and Fiest, 1980b).

As these organisms possess the enzyme systems to metabolize PAH compounds, the absence of PAH in general in some samples or specific PAH compounds in samples with petrogenic residues only indicate that the unmetabolized material is absent. Metabolic intermediates of PAH compounds go undetected in the hydrocarbon-specific analytical program used here. There is strong indication that the shrimp samples are not coupled to the surface sediment with respect to petroleum hydrocarbon assimilation, while a strong link to sorbent pad-captured (suspended) material is suggested due to the prevalence of Group 1 (petrogenic) aromatics in both sample types.

At the heart of this "damage" assessment program is the proper selection and use of the analytical chemical tools to establish the range of Ixtoc and Burmah Agate oil compositions which might be encountered and to "overlay" these compositional criteria on environmental PHC assemblages. The results of this study point to the strengths of certain methods and the shortcomings of others in accomplishing these tasks. Ultraviolet fluorescence spectroscopy (UV/F) was determined to be a useful and cost-efficient technique for screening both sediment and tissue extracts for the possible presence of petroleum residues prior to more extensive and expensive analyses. However, significant background fluorescence from PAH components in sediments and from a 312-nm band-generating "interference" (nonhydrocarbon) in shrimp increases the detection limits of the UV/F oil analyses and must be considered in evaluations of results from UV/F analysis. Recent petroleum additions to the samples (although not readily noted in actual samples but explored in laboratory experiments) became readily discernible at the 0.1 ppm level for low UV/F background sediments, at the 2-5 ppm level for high UV/F background

sediments and at the 0.1-ppm level for normal UV/F background tissues. The 312-nm/350-nm band ratio proved quite useful in evaluating the shrimp UV/F results. However, very little information could be obtained on the source of any observed PHC residues from UV/F data alone, and false PHC-positive results (i.e., background pyrogenic PAH perceived to be recent petrogenic additions) were frequent. However, false-negative results (i.e., PHC residues present when not detectable by UV/F) would be a slim possibility using UV/F screening techniques.

One basic premise of the past BLM-benchmark chemistry studies has been that n-alkane concentrations are keys to determining post-OCS development environmental changes. We have shown here that the n-alkane character of oils changes significantly over time through microbial degradation processes, faster where nutrients are abundant, slower where nutrients limit microbial growth (Atlas, 1981). Ixtoc oil residues were, by the end of 1980, and presumably much earlier, depleted drastically in n-alkanes due to such degradation. Furthermore, only low levels of petroleum should be expected in offshore sedimentary environments as a result of a major spill of the types investigated here. Small increments of n-alkanes added to a significant background PHC assemblage (0.05-1 $\mu g \cdot g^{-1}$) already containing seasonally varying n-alkane compounds make the use of n-alkanes as petroleum markers and identifiers quite marginal in low-level pollution impact areas such as that studied here. Oil transported to the offshore benthos, if present, would be expected to eventually reside in depositional areas, sites of maximum n-alkane background levels as well.

There are also significant n-alkane background levels in marine organisms (e.g., shrimp) which thwart the evaluation of incremental additions and which themselves are often misassociated with petroleum. For example, Type 3 (Figure 2-49) assemblages contain very abundant smooth n-alkane distributions which are not petrogenic but most likely of a microbiological origin (Han and Calvin, 1965; Boehm, 1980).

N-alkanes are quite useful for oil identifications provided (1) no microbial alterations have occurred, (2) only evaporative weathering has affected the oil, (3) reference residues (i.e., documented as associated with a particular spill, not necessarily the unweathered wellhead or tanker "reference" samples) are available, or a proven weathering model is available to predict compositions (e.g., Boehm et al., 1981a), and (4) they are used in conjunction with other techniques. Both GC/MS-derived aromatic hydrocarbon information (P:DBT ratios) and stable isotope information are equally well suited in this case to support n-alkane data or, where alkane data are suspect or lacking, to achieve definitive identifications. Where possible all three techniques (n-alkane matching, P-DBT ratios; stable isotopes), or at least two, should be used in concert for both fingerprinting petroleum residues and for examining environmental samples for such residues. Other techniques such as gas chromatography using element specific (i.e., sulfur) detectors were unable here to sort out the molecular differences between Ixtoc, Burmah Agate and other observed residues especially in sediments impacted by chronic pollutants.

In sedimentary and biotic samples detailed aromatic compound profiling by capillary GC/MS proved to be the most useful and definitive tool. Stable isotope measurements on sediments are not fine-tuned enough to differentiate chronic pollution from recent input of petroleum or to identify petroleum in the presence of significant PHC backgrounds. On the other hand, multi-parameter isotope analyses yield extremely useful results in establishing the likely identities of water-borne oils where PHC backgrounds are not a factor. Although GC/MS-aromatic compound analysis and stable isotopes reinforced each other in the sorbent pad (high level) analysis and source-fingerprinted the Ixtoc residues present, stable isotope measurements alone might yield false-positive results, insofar as establishing the presence of recent oil in sediments, and are of little use in biotal measurements.

Of great potential use in monitoring sedimentary oil spill impacts are regressions of trace level ($\mu g \cdot g^{-1}$) compounds (e.g., total phenanthrenes) or gross parameters (e.g., total hydrocarbons) on high-level bulk geochemical parameters (e.g., total organic carbon). Previous studies have shown the effectiveness of monitoring the regressions because of their sensitivity to non-normal (i.e., pollutant; Boehm and Quinn, 1978; Boehm, 1978; Boehm and Fiest, 1980c) hydrocardon inputs. Again, in this study good correlations were obtained between TOC and total hydrocarbons, n-alkanes, and selected PAH compounds, illustrating that hydrocarbons in the sediments are geochemically distributed rather than due to specific recent pollutant inputs. These regressions then serve as sentinel relationships which can isolate new additional PHC inputs at the 10 $\mu g \cdot g^{-1}$ level and additional PAHs at the 10-20 $\mu g \cdot g^{-1}$ level.

Finally, the question arises as to the location of the massive amount of residual spilled oil material, only a fraction of which can be accounted for in the Gulf of Mexico. We suggest that the sorbent pad samples point to the presence of Ixtoc residues in the suspended/resuspended (nepheloid layer or flocculent layer) sediment system. Whereas these residues were not detectable in sediments using conventional sampling equipment and whereas such a sampling artifact has been noted in other studies (Boehm et al., 1982), it is possible that oil/resuspended material associations account for much of the spilled oil in a highly mobile nepheloid system throughout the Gulf of Mexico OCS and deep-water system. Furthermore, due to the relatively small U.S. shoreline impact versus the total quantity of oil passing through the OCS region on the surface, it can be hypothesized that the Ixtoc I and Burmah Agate oils have incrementally added to the considerable standing crop of the tar balls in the Gulf of Mexico.

2.5 Conclusions

The following conclusions outline the major findings of the chemical assessment segment of this study. They incorporate findings presented in more detail in Section 3 on "Stable Isotope" measurements.

1. The use of the combined techniques of capillary GC, capillary GC/MS and isotope mass spectrometry (MS) to obtain detailed molecular (GC and GC/MS) and atomic (isotope MS) information on the n-alkane, aromatic hydrocarbon (two to five rings) composition, and stable isotope (C,H,S) ratios of suspect oils and tars, enabled definitive Ixtoc/Burmah Agate match-no match conclusions to be drawn. This combined use was equally effective in eliminating false positive and false negative results from one of the three techniques.

2. With the availability of several weathered Ixtoc reference oils/tars, n-alkane compositional plots were effective in source-matching during the spill period (1979). When microbial degradation did take place, for example in the 1981 beached oil samples, and the n-alkane fingerprint was lost, the use of GC/MS based information (ratios of alkylated phenanthrenes to alkylated dibenzothiophenes) in conjunction with stable isotopic measurements were very effective in tracking older Ixtoc and Burmah Agate sourced oils.

3. Carbon isotope measurements on saturate and aromatic fractions were not alone sufficient to accomplish source-matching. Significant differences in the hydrogen isotope measurements of Ixtoc and Burmah Agate oils differentiated the two. False Ixtoc-positive determinations based on ^{13}C and ^{2}H were revealed by ^{34}S determinations on asphaltene residues.

4. An examination of surface sediment samples from the mid-spill (1979) and post-spill (1980) sample sets by a hierarchical analytical scheme involving ultraviolet fluorescence spectrometry, fused silica capillary gas chromatography, and computer-assisted gas chromatographic mass spectometry was successful in examining the sediment hydrocarbon assemblage and showed that no significant recent petroleum ($> 10\ ng \cdot g^{-1}$) additions from any identifiable spill source were present in the primary study area. Burmah Agate residues were detected at stations within the 20-30 km of the wreck site.

5. Sediments do contain widespread evidence of a geochemically distributed (i.e., covarying with increasing total organic carbon content and decreasing grain size) chronic pollutant source(s) dominated by highly degraded saturated hydrocarbon residues (i.e., no n-alkanes) and polynuclear (three to five rings) aromatic hydrocarbon residues ($1\text{-}100\ ng \cdot g^{-1}$ of individual components). Thus the South Texas OCS sediments are not pristine in terms of anthropogenic inputs.

6. Regressions of both gross chemical parameters (e.g., total hydrocarbons) and individual groupings (e.g., n-alkanes) or compounds (e.g., individual aromatic compounds) with total organic carbon levels define the STOCS geochemical environment. Changes in levels of these compounds or groupings.

caused by pollutant inputs (e.g., oil) will be most readily observed as deviations from the geochemical regression.

7. Ixtoc oil was present in the sorbent pad samples, apparently tied up in the suspended sediment material also captured in these samples. This significant finding indicates that there was Ixtoc oil in the "system," associated with mobile sedimentary material (nepheloid layers, or surface flocculent layer). An association of surface sediment with this suspended material is not definitely established nor is the presence of this suspended matter definitely linked to biological impact. However, this finding in this and other studies does point to the inadequacy of the sampling technique (Smith-MacIntyre grab) in spill studies.

8. Low-level petroleum impacts, noted in GC/MS-derived aromatic hydrocarbon searches, were a fairly common occurrence in the penaeid shrimp population. Many of the impacted shrimp were obtained north of the study area but STOCS shrimp contain petroleum aromatic hydrocarbon levels in the 10- to 50-ppb range. These observations plus those of a general chromatographic nature indicating unresolved envelopes (UCM) associated with chronic pollution are inconsistent with previous findings describing a pollution-free penaeid shrimp population. Nevertheless, only one sample taken from north of the STOCS region contained residues possibly linked to any known spill.

SECTION THREE

CHEMICAL ASSESSMENT - STABLE ISOTOPE ANALYSES

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SECTION THREE

CHEMICAL ASSESSMENT (STABLE ISOTOPES)

3.1 Introduction

The blowout of the Ixtoc I well in the Bay of Campeche, Gulf of Mexico, resulted in the largest release of oil in the history of the petroleum industry. From the initiation of the blowout on June 3, 1979 to its curtailment in March 1980, more than 0.5 million metric tons (530 million litres) of crude oil were released into the marine environment. From June to September of 1979 the oil moved in a northward direction and began impacting the coastal environments of Texas in August.

During the spill, the Department of Commerce (National Oceanic and Atmospheric Administration) funded a oceangraphic cruise (The Researcher/Pierce Ixtoc I Cruise) to obtain information regarding the chemical nature and physical behavior of the spill. As part of the program, Global Geochemistry Corporation was requested to explore the utility of stable isotopes in both the characterization and tracing of the oil. Based on some previous analyses of tracing beach tars to seepage sources it was felt that the stable isotope ratios (atomic composition) of the oil might serve as a mechanism for tracing the dispersed oil since when compared to the molecular analyses, the atomic composition of oils remained relatively constant with increased oil weathering. The approach of using both molecular distributions (GC and GC/MS) and isotope ratios have been used in the petroleum industry for correlating oils with their source and were found to complement and reinforce each other in differentiating sources and addressing the problems of migration and mixtures (Seifert, Molodowan, and Jones 1979). Similarly the atomic composition of tars and oiled sediments can serve as a tool either for screening samples for future detailed molecular analyses or for supporting conclusions drawn on the basis of the molecular results.

The initial investigations from the Researcher Cruise indicated that: (1) isotopic (atomic) change of the oil varied little with time when compared with the molecular analyses; (2) the carbon isotope ratio of the tars was similar to other oils found in the area; (3) the deuterium values of the tars were all similar to the value for the oil or heavier than -100 parts per thousand (ppt) (SMOW); (4) the sulfur content of the asphaltenes in mousse samples was lower and the corresponding isotope ratio heavier when compared to the tar samples, indicating selective weathering of the sulfur compounds during mousse formation (Sweeney, Haddad, and Kaplan 1980). Although carbon and sulfur isotopes have been used to correlate beach tars with seepage sources in Southern California (Hartman and Hammond, 1981), this initial study was the first attempt in using stable isotopes as means for tracing an oil spill. It was found that while an isotope measurement of a single element (eg. carbon) could point to multiple sources, a crossplot of two or more (hydrogen, carbon, sulfur) isotope ratios was quite useful in differentiating oils from the target spill.

The previous work has been extended during this study to include analyses of oils, tars, and sediment extracts collected from the coastal areas off Texas in an attempt to identify those oils associated with the Ixtoc I spill and to assess its impact on the sedimentary and corresponding biological communities in the Gulf of Mexico.

The carbon isotopic composition of crude oils has received considerable attention in attempts to clarify the origin of oil deposits. Most of the early studies have been recently summarized by Deines (1980).

Most oils show $\delta^{13}C$ values in the range from -21 to -32 ppt. The frequency distribution shows a slow rise from -20 ppt, a suggestion of bimodality, to a strong maximum at -28 to -29 ppt and a very sharp drop in frequency towards lighter $\delta^{13}C$ values. If, in the frequency distribution of marine sediments, those deposited under special conditions and showing very heavy $\delta^{13}C$ values are for the moment ignored, there is a certain degree of similarity in shape between the $\delta^{13}C$ frequency distribution of the organic carbon from marine sediments and that of petroleum, with a shift of the petroleum $\delta^{13}C$ frequency distribution towards lighter $\delta^{13}C$ values by about 3 ppt. Compared to older sediments, petroleum shows again a similar frequency distribution, but it is also systematically displaced towards lighter isotopic compositions with respect to it. Hence, petroleum is on the average isotopically slightly lighter than the kerogen in sediments. In the few cases where it has been studied, it has been found that this holds true also for oil and supposed source rock. In comparison with coal it appears that in spite of a considerable overlap of the distributions, petroleum (mode -27 to 30 ppt) shows on the average lower $\delta^{13}C$ contents than coal (mode -23 to 26 ppt).

Although the carbon isotopic composition of all oils combined covers more than 10 ppt, it has been found that within a particular oil field the carbon isotopic composition variations can be much more restricted (less than 1 - 2 ppt). Hence, in combination with other oil characteristics $\delta^{13}C$ measurements may be used to characterize and correlate oils and can represent a useful tool to the explorationist. Likewise, $\delta^{13}C$ determinations may be of help to trace the source of major oil spills.

As petroleum is a complex mixture of organic compounds part of the variability in the $\delta^{13}C$ values of petroleum might be related to carbon isotopic composition differences between the different chemical components of crude oil. There have been relatively few studies in which separated chemical compounds or compound groups have been analyzed. In some of these only very small $\delta^{13}C$ differences between petroleum fractions were observed, while in others, systematic trends in $\delta^{13}C$ variations were discovered. Asphaltenes, which contain the highest molecular weight molecules, and tars show a slight $\delta^{13}C$ enrichment with respect to the total oil; wax and paraffin, containing somewhat lower molecular weight molecules show a slight $\delta^{13}C$ depletion with respect to the total oil. For the gaseous components butane, propane, ethane and methane the $\delta^{13}C$ depletion increases with decreasing molecular weight. Another feature worth noting is that in most of the oils studied the saturates are systematically depleted in $\delta^{13}C$ with respect to the aromatic compounds.

Few D/H ratio measurements have been recorded for petroleum. Four

Middle East crude oils were measured by Schiegl and Vogel (1970) and they report an average δD value of -89 ppt. More recently, D/H measurements on fifteen Paleozoic oils from Michigan, U.S.A., yielded a δD range of -90 to -130 ppt (Brand et. al., 1980). In this latter study it was determined that the paraffin fraction was approximately 10 ppt lighter than the aromatic fraction.

In a very recent study, Yeh and Eptein (1981) report data of D/H and $\delta^{13}C$ for 114 petroleum samples and for several samples of related organic matter. δD of crude oil ranges from -85 to 181 ppt, $\delta^{13}C$ of crude oil ranges from -23.3 to -32.5 ppt. Variation in δD and $\delta^{13}C$ values of compound-grouped fractions of a crude oil is small, 3 and 1.1 ppt, respectively, and the difference in δD and $\delta^{13}C$ between oil and coeval wax is slight. Gas fractions are 53 - 70 and 22.6 - 23.2 ppt depleted in δD and $\delta^{13}C$, respectively, relative to the coexisting oil fractions. The δD and $\delta^{13}C$ values of the crude oils appear to be largely determined by the isotopic compositions of their organic precursors.

3.2 Methods and Approaches

Samples of tars and sediments were fractionated at ERCO into saturate and aromatic fractions and received by Global Geochemistry Corporation for sulfur, carbon, and hydrogen isotope analyses. For the majority of the sediments the saturate and aromatic fractions had to be combined to yield enough material for isotope measurement. Approximately one (1) milligram of sample was combusted at 900°C in the presence of cupric oxide and silver metal (Stump and Frazer, 1973). The produced CO_2 was purified and collected for isotope analysis. The water from combustion was converted to molecular hydrogen by reaction with uranium turnings at 800°C, collected on activated charcoal under liquid nitrogen, and transferred to a break-seal tube via a Toeplar pump.

Approximately 0.5 grams of the asphaltenes from the tar and oil samples were combusted in a Parr Bomb in 30 atmospheres of oxygen with the produced sulfate precipitated as $BaSO_4$ (Parr Instrument Company, 1965). Sulfur dioxide was prepared for isotopic analysis by direct combustion of the barium sulfate with quartz powder at 1200°C (Bailey and Smith, 1972).

The stable isotope ratios for carbon were determined on a Nuclide 3" - 60° RMS instrument, the hydrogen on Varian MAT 250, mass spectrometer, and the sulfur on Nuclide 6" - 60° RMS mass spectrometer. All isotopic data are expressed in the standard δ notation:

$$\delta x \text{ sample (ppt)} = \frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}} \times 1000$$

where x represents the element and R the ratio of the rare to abundant isotope of that element. Values for carbon are relative to the Chicago Pee Dee Beleminite (PDB), those for hydrogen are referenced to standard mean ocean water (SMOW), and the sulfur isotopes are relative to the Canyon Diablo Troilite. Precision for carbon, hydrogen, and sulfur are 0.10 ppm, 1.0 ppm, and 0.3 ppm, respectively.

3.3 Results

The fractions of thirty-four oil and tar samples were analyzed for their C,H, and S isotope ratios and four sorbent pads for C and H isotope ratios (Table 3-1). Additionally, thirty-one sediment extracts were also analyzed for C and H isotope ratios to determine the extent of oil contamination in the coastal sediments (Table 3-2).

Both oil and sediment samples represent two collection periods during late 1979 and late 1980. All the sediment and tar samples were collected on the Southeast coast of Texas from Galveston Bay to the Mexican border. These collections included a suite of samples obtained when the Burmah Agate tanker spilled and burned its cargo during mid 1979. The Burmah Agate oil sample collection is designated as samples 9-15, and 23 and the sediments as 32, 33, and 34.

The $\delta^{13}C$ values of the saturate hydrocarbons for the tar samples ranged between -27 ppt to -28 ppt (PDB). For the 1979 samples, the Burmah Agate collection of oils is generally heavier (greater δ^{13} content) than -27 ppt and the Ixtoc I oils are lighter than -27.5 ppt. The 1980 Ixtoc I oils are about 0.5 ppt heavier than those collected in 1979 (Figure 3-1 and 3-4). The deuterium values of the Ixtoc I saturates range between -80 and -100 ppt (SMOW) with the 1980 samples slightly heavier than those collected in 1979 (Figure 3-1). The deuterium values of the Burmah Agate saturates are about 20 ppt lighter than those related to Ixtoc I, ranging between -110 and -120 ppt (SMOW). Three samples from the Burmah Agate suite (1, 9, 14) have a deuterium content similar to the Ixtoc I samples.

The $\delta^{13}C$ values for the aromatic fractions of the Burmah Agate oils are heavier than the Ixtoc I samples by about 0.5 ppt; and the deuterium of the Burmah Agate tars is depleted by about 20 ppt relative to Ixtoc I samples (Figure 3-2).

A plot of the $\delta^{34}S$ values of the asphaltenes versus the $\delta^{13}C$ of the aromatic fraction indicates that the Burmah Agate related oils are isotopically heavier for both carbon and sulfur relative to samples suspected of being Ixtoc I sourced (Figure 3-3).

As indicated by the other isotope crossplots, a carbon vs. carbon plot of the saturate and aromatic fractions show the tars and oils separated into three groups: Ixtoc I, Burmah Agate, and unrelated sources (Figure 3-4). The separation of the groups is largely controlled by the $\delta^{13}C$ of the aromatic fraction.

The saturate fraction of four sorbent pads (samples 35 - 38, Table 3-1) was analyzed for its carbon and hydrogen isotope ratios. As the data indicate, samples 35 and 38 would fall in the Ixtoc I compositional "window" with the isotope ratios of samples 36 and 37 being much too heavy to be Ixtoc I sourced.

As previously mentioned, for a large number of the sediment samples,

Table 3 1

CARBON, HYDROGEN, AND SULFUR ISOTOPE DATA FOR THE TARS, OILS, AND SORBENT PADS.

GGC#	SAMPLE # (BLM)	F_1		F_2		F_3	PROBABLE
		$\delta^{13}C$	δD	$\delta^{13}C$	δD	$\delta^{34}S$	SOURCE
1	7911-P02-1001	-27.13	-96	-26.54	-91.7	3.82	Bur. Ag.
2	7912-P20-1001	-27.54	-83	-27.3	-93	-2.31	Ixtoc
3	7912-P24-1001	N.D.	N.D.	-27.33	-94.3	-2.54	Ixtoc
4	7911-P06-1001	-27.9	-95.1	-27.25	-87.9	-4.72	Ixtoc
5	7911-P09-1001	-27.83	-88.6	-27.12	-90.5	-.27	Ixtoc
6	7912-P12-1001	-27.84	-93.4	-27.29	-93.2	2.31	Ixtoc
7	7908-I4C-1001	-27.6	-94.4	-27.27	-92	-5.18	Ixtoc
8	7908-I5A-1001	-27.71	-92	-27.24	-90.1	-3.86	Ixtoc
9	7911-B04-1001	-27.85	-91.6	-26.85	N.D.	3.50	Bur. Ag.
10	7911-B02-1001	-27.43	N.D.	-26.54	-117.3	7.46	Bur. Ag.
11	7911-B02-1002	-27.37	-114.8	-26.62	-114.5	5.74	Bur. Ag.
12	7911-B07-1001	-27.38	-115	-26.31	-108	4.92	Bur. Ag.
13	7911-B03-1011	-27.27	-118	-26.28	-78	2.54	Bur. Ag.
14	7911-B01-1011	-27.29	-98	-26.47	-114	4.59	Bur. Ag.
15	7911-B04-1002	-27.76	-118	-26.53	-103	10.06	Bur. Ag.
16	8012-T01-1001	-27.28	-91	-27.07	-90	-3.79	Ixtoc
17	8012-T02-1001	-27.32	-100	-26.68	-90	-.70	Unknown
18	8012-T03-1001	-27.31	-92.4	-26.66	-87.5	.02	Unknown
19	8012-T04-1001	-27.18	-89	-26.91	N.D.	N.D.	Unknown
20	8012-T05-1001	-27.10	-90	-26.90	-94	-5.45	Ixtoc
21	7908-CM2-1001	-27.43	-83.8	-27.07	-91.4	-3.06	Ixtoc
22	7911-B05-1001	-27.40	-118	-25.87	-125	4.81	Unknown
23	7911-B06-1001	-27.46	-118	-26.47	-111	-4.13	Bur. Ag.
24	7908-Q05-1001	-28.95	-108	-28.28	-112	3.11	Unknown
25	7908-CM1-1001	-27.46	-89	-27.06	-83	-2.21	Ixtoc
26	8004-E02-1001	-27.28	-86.9	-27.10	-73.2	-3.61	Ixtoc
27	8004-E03-1001	-27.41	-85.5	-27.08	-75.7	-.22	Ixtoc

28	8004-E04-1001	-27.39	-83.4	-27.08	-86.8	-3.65	Ixtoc
29	8004-E05-1001	-27.29	-80.6	-27.97	-75.5	-5.24	Unknown
30	8004-E01-1001	-27.33	-81.4	-27.09	-81.8	-4.02	Ixtoc
31	7908-Q01-1001	-27.54	-80.8	-27.89	-78.5	1.86	Unknown
32	7908-Q02-1001	-27.47	-123.0	-24.94	-121.7	3.91	Unknown
33	7908-Q03-1001	-27.62	-79.0	-27.05	-74.7	3.67	Unknown
34	7908-Q04-1001	-27.06	-79.4	-27.63	78.2	-6.44	Unknown
35	7911-S46-1001	-27.39	-90	N.D.	N.D.	N.D.	Ixtoc
36	7911-M25-1001	-22.46	-45	N.D.	N.D.	N.D.	Unknown
37	7911-S27-1001	-23.86	-30	N.D.	N.D.	N.D.	Unknown
38	7911-S21-1001	-27.31	-99	N.D.	N.D.	N.D.	Ixtoc

N.D. Not Determined

Table 3-2

CARBON AND HYDROGEN ISOTOPES FOR THE SEDIMENT EXTRACTS

		SATURATE (F_1)		AROMATIC (F_2)	
GGC	BLM I.D.	$\delta^{13}C$	δD	$\delta^{13}C$	δD
1	7909-R23-6001*	-26.66**	--	--	--
2	7912-PA2-6001*	-25.96	-51	--	--
3	7912-M04-6001*	-25.37	--	--	--
4	7912-M14-6001*	-26.03	-0.2	--	--
5	7911-M21-6001*	-25.90	-26	--	--
6	7912-M05-6001	-27.01	-90	-23.17	--
7	7911-M35-6001*	-26.78	-75	--	--
8	7912-M37-6001	-19.82**	--	-20.74	-7
9	7911-S06-6001*	-24.15	--	--	--
10	7912-N39-6001*	-26.31	-34	--	--
11	7911-S53-6001*	-21.35**	+11	--	--
12	7912-N38-6001	-27.18	-58	-25.30	-63
13	7912-S51-6001*	-25.85	-30	--	--
14	7911-S53-6001*	-25.10	-21	--	--
16	8012-N39-6001*	-25.89	-30	--	--
17	8012-S52-6001*	-22.09**	-12	--	--
18	8012-S51-6001*	-27.13**	-70	-21.02	-28
20	8012-M36-6001	-26.92**	-75	-20.23	--
21	8012-S31-6001	-27.36**	-80	-23.45	--
22	8012-M35-6001	-23.57	--	-25.97	-75
23	8012-N38-6001*	-26.46	-34	--	--
25	7911-S52-6001	--	--	--	--
26	7911-S54-6001*	-20.67**	-67	--	--
27	7911-S50-6001*	-23.95	-56	--	--
28	7911-S31-6001*	-23.98	-28	--	--
29	7911-S26-6001*	-20.49**	-22	--	--

30	7911-S29-6001*	-24.76	-133	--	--
31	8012-N37-6001*	-26.89	-157	--	--
32	8012-G04-6001	-27.28	-101	-25.74	-107
33	8012-G05-6001	-25.90	-70	--	--
34	8012-G06-6001	-24.83	-58	-24.87	-62
35	7909-ANC-6001	-22.54	-55	-25.71	-60

**Small sample, data may not be reliable

*Analysis of combined F_1 and F_2 fractions

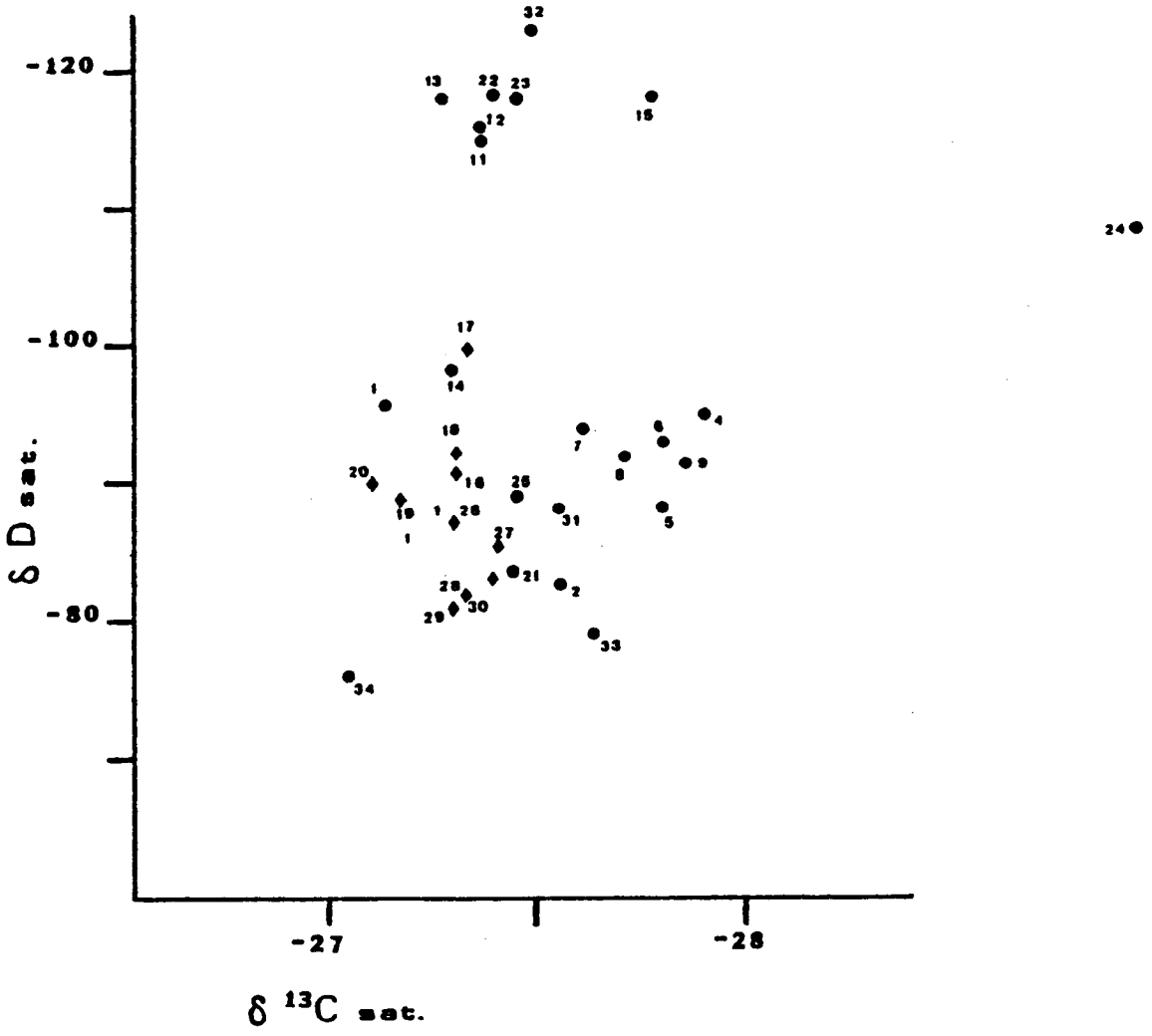

Figure 3—1. Carbon, Hydrogen, and Sulfur Isotope Data for the Tars, and Sorbent Pads (● 1979 Samples and ◆ are 1980 Samples).

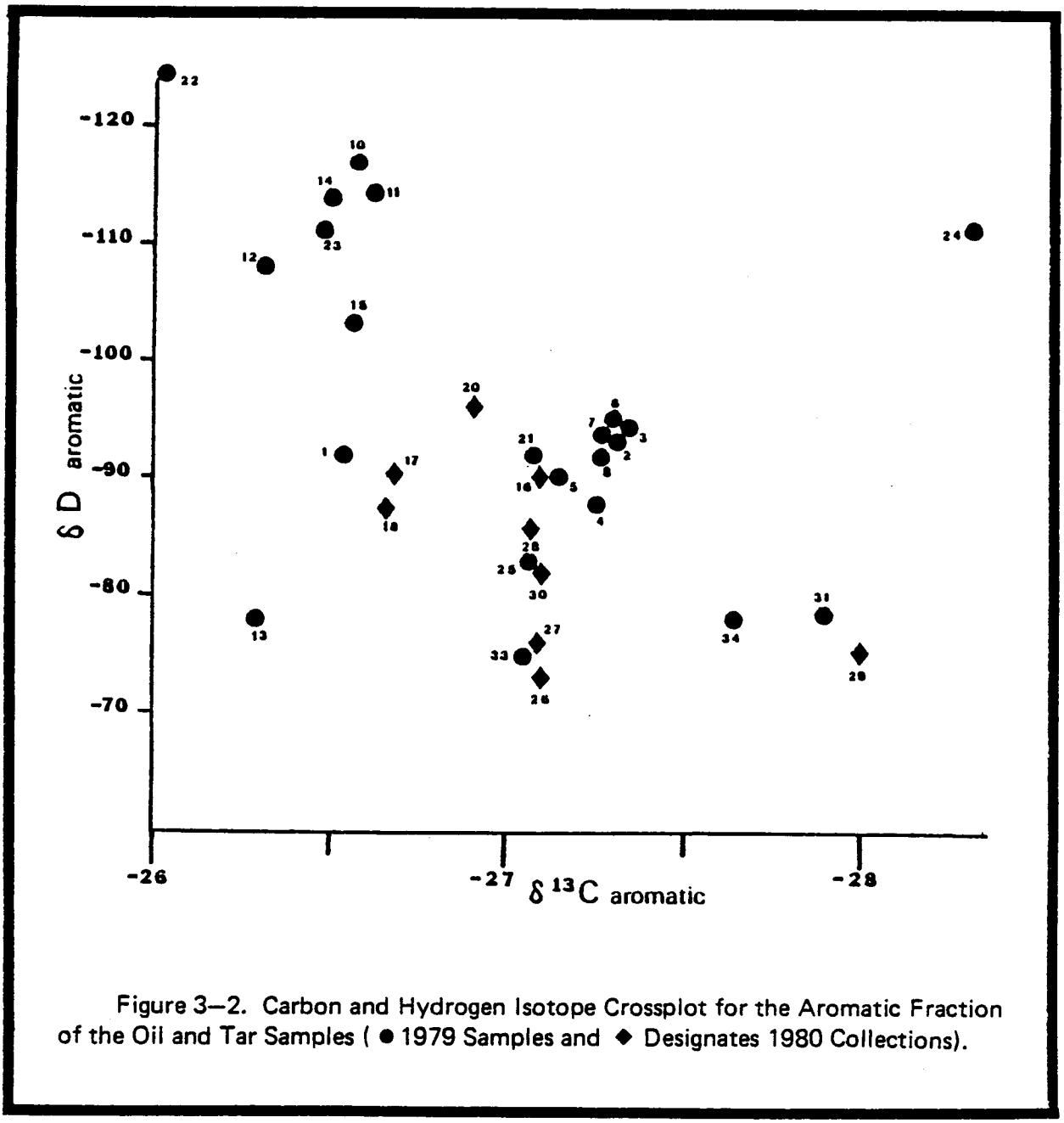

Figure 3—2. Carbon and Hydrogen Isotope Crossplot for the Aromatic Fraction of the Oil and Tar Samples (● 1979 Samples and ◆ Designates 1980 Collections).

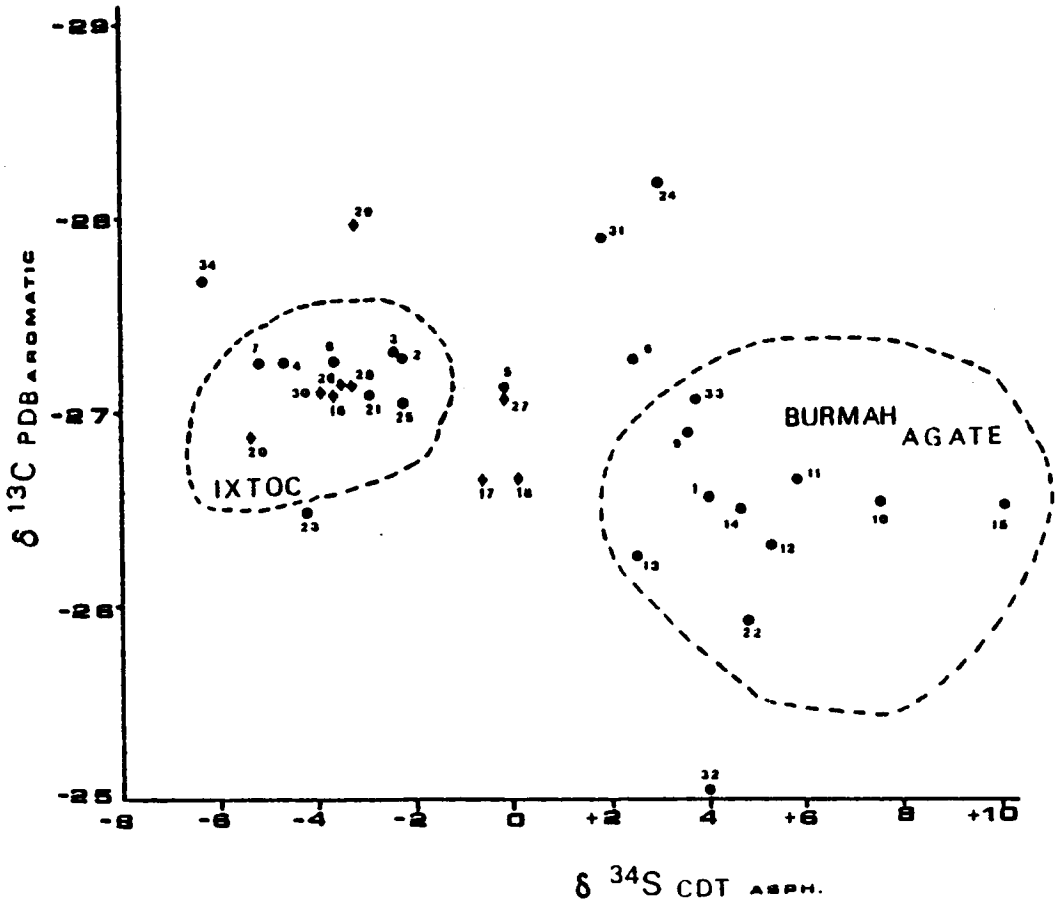

Figure 3–3. Crossplot of the Carbon Isotopes of the Aromatic Fraction Versus the $\delta^{34}S$ of the Asphaltenes from Tars and Samples (● 1979 Samples and ◆ Designates 1980 Samples).

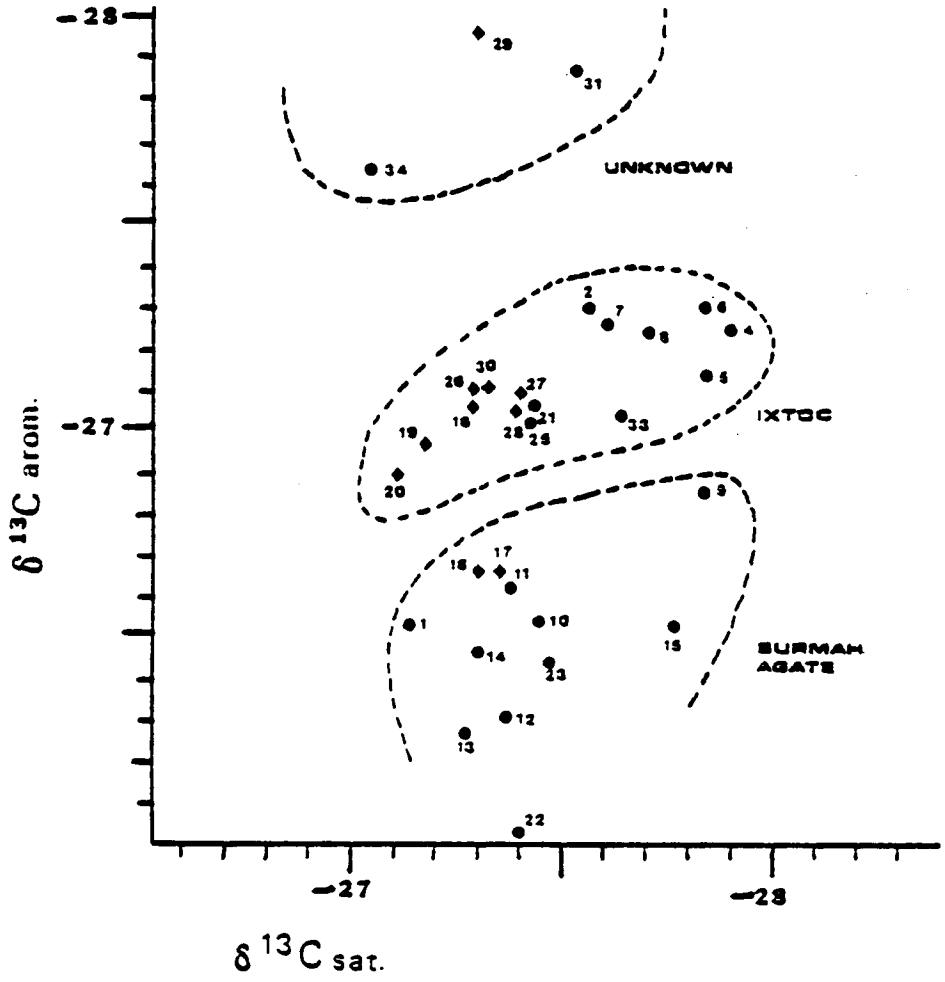

Figure 3—4. Crossplot of the $\delta^{13}C$ for the Saturate and Aromatic Fraction for the Tars and Oils (● 1979 Samples, ◆ 1980 Samples).

the saturate and aromatic fractions were combined to yield sufficient material for isotope analyses. The data for these samples are listed in Table 3-2 and illustrated in Figure 3-5.

Even with the combination of fractions some samples were so small that the isotope values obtained may not be accurate. These samples are indicated in Table 3-2 and were excluded in the plot of the data (Figure 3-5).

While general trends are difficult to establish for the sediments as a whole, paired comparisons of 1979 with 1980 collections can be made for certain stations. For both Stations S51 and S31 the 1980 samples are isotopically lighter, suggesting a greater degree of petroleum contamination in the 1980 collection. For Station M35, the isotope data of the 1979 sample represents both aromatic and saturate fractions; whereas, for the 1980 collection, only the aromatic fraction was measured. Since the deuterium values are similar, the data probably indicate that either little change or a slight decrease in the degree of contamination has occurred during 1980, even though the $\delta^{13}C$ value is approximately 1 ppt lighter for the 1979 collection. The isotopic data for Station N-39 are isotopically heavier for the 1980 sample indicating that a small decrease in the level of sediment petroleum has occurred with time. The same trend appears to have taken place for Station N-38, although, as in most cases, the comparison is between a saturate fraction for the 1979 sample and combined fractions for the 1980 sample.

The sediments collected from the Burmah Agate stations (32, 33, 34) show a progressive increase in the ^{13}C and deuterium content of the saturate fraction with increased distance from "source", corresponding to a decrease in contamination in a southwest direction.

3.4 Discussion

In this investigation, the carbon and hydrogen isotope ratios of hydrocarbon fractions from collected tars and sediments were determined along with the sulfur isotope ratios of the tar and oil asphaltenes. In using isotope crossplots, oils sourced from the Ixtoc I can be easily differentiated from other sources such as the Burmah Agate samples. For those oils suspected of being Ixtoc I sourced, the samples collected in 1980 are isotopically heavier than those collected a year earlier. Whereas this fractionation may result from increased weathering which selectively removes the lighter isotope, compositional variation of the source oil can not be discounted. In the earlier work on Ixtoc I (Sweeney, Haddad, and Kaplan 1980), the carbon isotopes of a certain fraction of the tars collected near the wellhead were isotopically heavier than the oil by about 0.5 ppt indicating either compositional variation in the source or rapid differential weathering.

Due to the difficulty in obtaining adequate sample sizes for the sediment hydrocarbons, detailed temporal and spatial analysis was not possible. As a result of the small samples, many of the isotope measurements had to be performed on combined saturate and aromatic fractions. Data comparisons based on these various fractions may therefore not be as rigorous as would be desired. Nevertheless, those samples

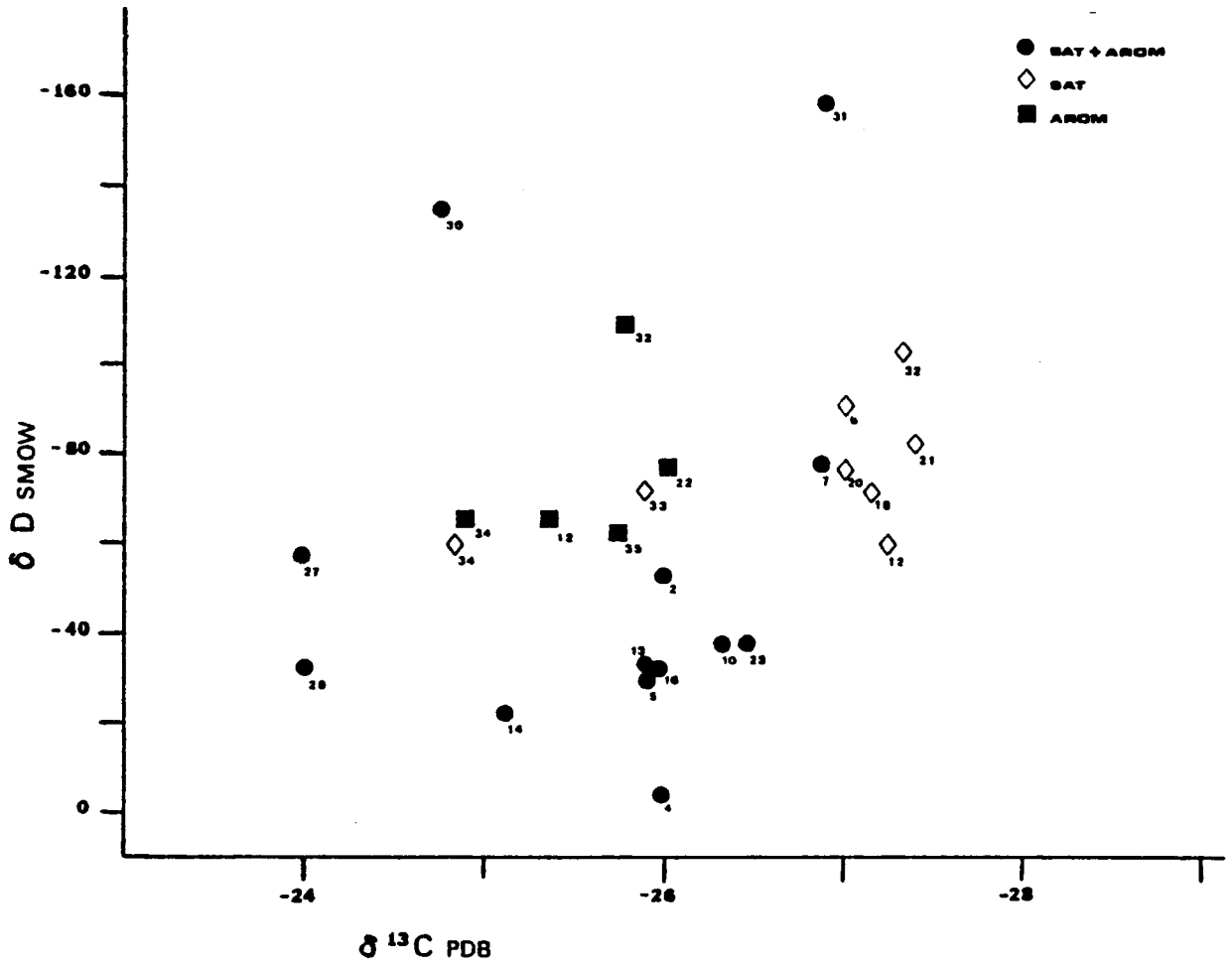

Figure 3—5. Carbon and Hydrogen Isotope Plot for the Sediments Extracts.

displaying $\delta^{13}C$ values lighter than -26 ppt and deuterium lighter than -60 ppt (SMOW) appear to be contaminated with petroleum-sourced material. This is readily apparent in viewing the Burmah Agate transect (sample 32, 33, 34).

3.5 Conclusion

The isotope ratios of carbon, hydrogen, and sulfur are useful in differentiating oils from various sources. Even upon extensive weathering which effects large changes in the molecular composition, the atomic ratios remain remarkably constant. In this study most of the tars could be definitively grouped into either Ixtoc I, Burmah Agate, or unrelated with a few tars possibly being mixtures.

The isotopic results from the sediment extracts are not as easily explained as those from the tars. The analyses (and consequent interpretation) was hampered by inadequate sample size. Furthermore, a baseline knowledge of the hydrocarbon isotope ratios of sediments was not available, so that determining the level of contamination in a system with differing degrees of terrestrial, pelagic, and anthropogenic deposition is difficult. However, in those samples which had adequate material for valid comparisons to be made, the temporal change in the "degree" of contamination could be assessed.

It has been demonstrated in this study and previous work that stable isotope analyses are a useful tool in sourcing an oil from seepage as well as a spill. In either case at least two isotope ratios are required for resolving oil populations. Relative to molecular distributions, the atomic ratios of oils vary little with the degradation experienced during a spill situation. In the case of widespread dispersal in areas of seepage or industrial development, stable isotope ratios can be a relatively low cost method of screening an oil, tar, or mousse sample for its probable source.

In areas such as the Gulf of Mexico where the retention capacity of the sediments maybe low (i.e. coarse grained sediments) larger extractions need to be performed to yield sufficient material for analyses. Also, in shallow waters where both bioturbation and/or storm activity can rapidly bury or remove the fine particles of sedimented oil, stable isotope as well as molecular analyses may serve little utility in damage assessment efforts. In these "high energy" environments, chemical tracing techniques may be useful only if the time between the event and sediment sampling are relatively short.

SECTION FOUR

BIOLOGICAL ASSESSMENT

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BIOLOGICAL ASSESSMENT

4.1 Introduction

On June 3, 1979, an exploratory petroleum well named Ixtoc I being drilled by Petroleos Mexicanos in the Gulf of Campeche, Mexico, blew out uncontrollably. The well gushed oil until late March, 1980, when it was finally capped. The accident was the largest spill to date by far in the Gulf of Mexico, releasing approximately $5.3 \times 10^5/m^3$ of crude oil into the ocean. Oil from Ixtoc I apparently weathered rapidly near the wellhead and then moved northward on the surface and beneath it. About 4,350 m^3 of oil were deposited on south Texas beaches during the spill (Gundlach et al. 1981); however, the quantity of oil reaching the benthos is completely unknown. The south Texas shelf is nearly all unconsolidated sediment, ranging from sand nearshore to predominantly clay and sandy and silty clay offshore (Flint and Holland 1980, Gallaway 1981).

By coincidence, part of the area believed to be exposed to petroleum from the Ixtoc I spill had been subjected to an extensive environmental study during 1975, 1976, and 1977, under the sponsorship of the U.S. Bureau of Land Management (BLM). For many years, "baseline" outer continental shelf studies sponsored by the Bureau of Land Management (BLM) have had as their avowed purpose to describe biological conditions, so that in the event of an environmental catastrophe (e.g. an oil spill), the extent and nature of the impact might be understood by comparison to the previous situation. The value of such a damage assessment program would depend upon its ability to determine if damage were, in fact, detected and assigned beyond a reasonable doubt to its proper cause. The South Texas Outer Continental Shelf (STOCS) baseline study program included a wide variety of environmental measurements designed to meet BLM needs for impact assessment should the area be leased for future petroleum development. A large number of intertidal and subtidal sites were studied along the south Texas shelf, which is nearly all unconsolidated sediment ranging from sand nearshore to mud (predominantly clay) offshore (Flint and Holland 1980, Gallaway 1981). Among the subtidal biological communities surveyed, the macroinfauna (defined as soft-bottom organisms retained on a 0.5 mm screen) was characterized in the STOCS program as being relatively stable, showing a lack of pronounced seasonal fluctuations (Holland et al. 1980).

In light of this supposed stability, and in part as a result of the STOCS use of repeatable, standardized methods for benthic sampling, the BLM sponsored a study of the macroinfaunal community during the Ixtoc I spill (November 1979) and one year later (December 1980). Benthic samples were taken at 12 of the same STOCS sites using the same methods previously employed in the STOCS project. The samples were subjected to biological, chemical and sedimentological analyses to determine whether or not any effects of the Ixtoc I spill on the macroinfauna might be detected.

The circumstances under which this study was undertaken could not practically be expected to have been better. The oil spill was massive; there was a large amount of baseline biological data on the area; and the methods used in the baseline study were standardized and repeatable. In some senses, this study was the first test of the utility of the baseline concept for petroleum impact assessment, since until the Ixtoc I spill no such human-caused catastrophe had occurred in an area previously included in a comprehensive baseline program.

This report describes the results of the benthic biological study, while the chemical and geological results are presented in Sections 2, 3, and Appendices 9.1 and 9.2. The 1979 samples were taken by a multi-agency "Regional Response Team" (NOAA 1982) while the 1980 samples were collected by LGL Ecological Research Associates, Inc. and by Energy Resources Company, Inc. (ERCO). Analysis of 1979 and 1980 biological samples and data was performed by LGL, while ERCO was responsible for chemical sample and data analysis. Geomet Technologies, Inc. analyzed the sediment samples for texture.

The 1980 sample collection included benthic material from 28 additional stations not previously sampled for biological parameters. Two of these stations were very near the site of the 1979 collision of the oil tanker Burmah Agate with a freighter, which resulted in a spill of over 3.4×10^4 m^3 and a subsequent fire near the Galveston, Texas harbor entrance (Kana and Thebeau 1980). Since the data from these 28 stations cannot be compared to equivalent biological data from any other sampling periods, the results from these stations will be discussed separately in Appendices 9.3.1 and 9.3.2.

4.2 Methods and Approaches

4.2.1 Sampling

Benthic samples were collected with a Smith-McIntyre 0.1 m^2 grab. Six grabs were taken for biological and sediment samples at each of 12 stations (three each on four transects running roughly perpendicular to the beach) selected by the BLM (Figure 4-1, Table 4-1) and an additional grab furnished chemical and sediment samples. Station numbers used in the STOCS program were retained for continuity. The biological grab samples were sieved through 0.5 mm screen on board, and biota preserved in 5-10% neutral buffered formalin and dyed with rose bengal to highlight animals during the sorting process in the laboratory.

4.2.2 Analytical

A total of 72 grab samples from 1979 and 72 from 1980 collections (12 stations x 6 replicates for each year) were analyzed in the laboratory. Analysis included identification and enumeration of all individuals to the lowest possible taxon. All species identified were independently verified by specialists outside LGL. Many species (especially those for which

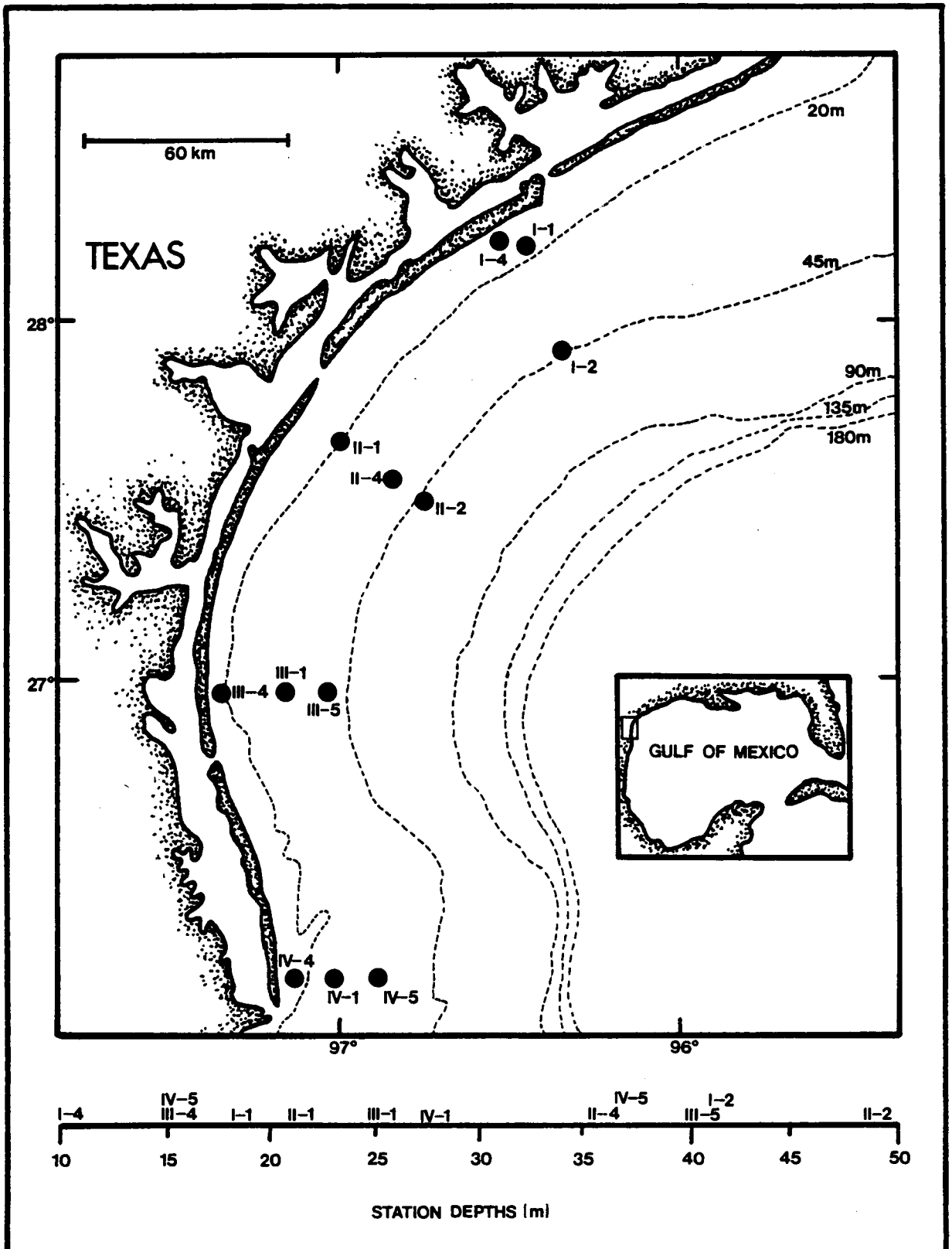


Figure 4-1. Map of 12 STOCS and LGL/ERCO stations.

Table 4-1. Station locations and depths.

BLM/STOCS STATION NUMBER	DEPTH (m)	LATITUDE (N)	LONGITUDE (W)
I-4	10	28°14'	96°29'
I-1	18	28°12'	96°27'
I-2	42	28°14'	96°29'
II-1	22	27°40'	96°59'
II-4	36	27°34'	96°50'
II-2	49	27°30'	96°45'
III-4	15	26°58'	97°20'
III-1	25	26°58'	97°11'
III-5	40	26°58'	97°02'
IV-4	15	26°10'	97°08'
IV-1	27	26°10'	97°01'
IV-5	37	26°10'	96°54'

current taxonomy is incomplete or in dispute) were verified by the same personnel responsible for identification of the STOCS samples, to ensure continuity between the LGL study and the baseline research.

It was not always possible to identify each taxon to the species level, as a number of previously undescribed species, or damaged or incomplete individuals or immature forms were collected. In several groups of organisms, taxonomic problems and limitations on resources precluded detailed identification during both the STOCS and the LGL programs. It was necessary to prevent taxa which were, e.g., previously grouped together from seeming suddenly to become common and the group to become absent, or vice versa. Whenever appropriate, therefore, taxa were grouped per STOCS identifications in statistical analyses comparing different sampling periods, to avoid spurious appearances or disappearances. A permanent reference collection was prepared from the 1979 and 1980 samples for deposit in the U.S. National Museum to aid in future taxonomic clarification.

Taxa that were present in the samples but known to be macroinfaunal incidentals, such as (wholly planktonic forms) and various fish (which were not collected qualitatively by the sampling methods used) were not included in the statistical analyses (Table 4-2).

While it would have been ideal to compare samples taken at each station at the same time of year, the 1976 and 1977 STOCS winter and fall samples were taken during January-February and September-October, respectively, and the 1979 and 1980 samples were collected in November and December, respectively. The chronology was, thus, winter 1976, fall 1976, winter 1977, fall 1977, November 1979, and December 1980. The month of collection is specified for 1979 and 1980 samples throughout the report (rather than "winter" to avoid confusion with the 1976 and 1977 STOCS winter samples, which did not directly overlap the 1979 and 1980 collection periods. The number of replicate grabs taken during the first year of the STOCS program was also not equivalent to later samples (four vs. six). Since the STOCS data indicated "significant temporal variation...in numbers of individuals" (Holland et al. 1980), statistical comparisons were restricted to 1980, 1979, and fall and winter 1977 and 1976 samples.

Statistical analyses included comparisons between sampling periods within stations, and comparisons between stations within sampling periods. Correlation analyses were performed on a taxon-by-taxon basis with sediment texture indices and total organic carbon (TOC) for all sampling periods in which TOC values were available in the STOCS data base. Cluster analyses were used to elucidate groupings of taxa, stations and time periods, and sediment types.

Table 4-2. Checklist of invertebrate taxa believed to have been incidentals or not macroinfauna (e.g. planktonic forms) and fish, consequently omitted from data analysis for 1979-1980 samples.

PHYLUM ARTHROPODA
- CLASS Crustacea
  - SUBCLASS Copepoda
    - Order Calanoida
      - *Acartia danae*
      - *Acartia tonsa*
      - *Acrocalanus longicornis*
      - *Aetidius armatus*
      - *Calanopia americana*
      - *Candacia curta*
      - *Centropages velificatus*
      - *Clausocalanus furcatus*
      - *Euatideus giesbrechti*
      - *Eucalanus pileatus*
      - *Heterorhabdus papilliger*
      - *Labidocera aestiva*
      - *Labidocera* cf. *scotti*
      - *Lucicutia flavicornis*
      - *Paracalanus crassirostris*
      - *Temora stylifera*
      - *Temora turbinata*
    - Order Cyclopoida
      - *Corycaeus speciosus*
      - *Sappharina nigromaculata*
    - Order Caligoida
      - *Caligus* sp.
  - SUBCLASS Malacostraca
    - Order Amphipoda
      - Hyperiidae
      - *Hyperia spinigera*
    - Order Euphausiacea
      - *Thysanopoda orientalis*
    - Order Decapoda
      - Sergestidae
        - *Lucifer faxoni*
      - Oplophoridae
        - Miscellaneous larval oplophorids (unid.)
      - Stenopodidae
        - Miscellaneous larval stenopodids (unid.)
        - Miscellaneous larval brachyurans (unid.)
        - Miscellaneous larval anomerans (unid.)
      - Albuneidae
        - Miscellaneous larval *Albunea* spp.

PHYLUM CHORDATA
- CLASS Hemichordata
  - Hemichordate (unid.)
- CLASS Cephalochordata
  - *Branchiostoma caribaeum*

Table 4-2 (cont'd)

CLASS Vertebrata

- Muraenidae
  - *Gymnothorax nigromarginatus*
- Congridae
  - *Neoconger mucronatus*
- Ophichthidae
  - *Echiophis* sp.
  - *Ophichthus gomesi*
- Bregmacerotidae
  - *Bregmaceros atlanticus*
- Ophidiidae
  - *Lepophidium graellsi*
- Sciaenidae
  - *Micropogon undulatus*
- Gobiidae
  - *Gobiosoma longipala*
- Microdesmidae
  - *Microdesmus lanceolatus*
- Cynoglossidae
  - *Symphurus* sp.

The biological data were not normally distributed, and the large amount of heterogeneity present in the data set led to significant first-, second-, and third-order interaction terms in parametric analyses of variance (ANOVA's). Consequently, comparison tests for central tendency (e.g. median abundance of taxa within stations over time) were restricted to nonparametric procedures such as the Kruskall-Wallis one-way and Friedman two-way ANOVA's (Friedman 1937, Kruskal and Wallis 1952). Kendall's Tau was used for correlation analyses (Kendall 1938). Czekanowski's Quantitative Index (= Bray-Curtis Index) was used to assess similarity in the cluster analyses, as it accurately describes overlap without regard to data distribution (Bloom 1981). Community summary statistics included the Shannon-Weaver function based on natural logs (Shannon and Weaver 1949) as a diversity index (H'), and Fager's (1972) scaled form of H', called V' by Pielou (1977) to describe evenness. Although somewhat less familiar than Pielou's (1966) evenness index J', V' is more appropriate than J' for comparison of samples with different numbers of individuals and taxa. As a practical matter, V' and J' typically respond similarly to community changes.

It was necessary to reduce the number of taxa during data analysis to statistically tractable and conceptually manageable proportions. The great majority of the 576 taxa seen during the STOCS program and in the 1979 and 1980 samples were rare, represented by single appearances or very low abundances. The entire data set included 65,166 individuals. The decision was made to focus attention on a restricted set of numerically dominant taxa. A rarefaction curve (Figure 4-2) demonstrated that 72 of these taxa (12.5% of the 576 taxa seen) included 56,584 individuals, 87% of the total, using a minimum cutoff level for inclusion of 0.2% of 65,166 (i.e., 130 individuals). Even a rather more restrictive inclusion cutoff level of 1% of 65,166 (i.e. 651 individuals) excluded all but 18 taxa (3% of the 576 taxa seen) and still included 39,999 individuals, 61% of the total. Numerically dominant taxa were arbitrarily defined by use of these two cutoff points: 0.2% of the total overall 65,166 for analyses which included all stations and sampling periods, and 1% of the total at each station for station-by-station descriptions. Figures based on either cutoff bear the notations "1% cutoff" or "0.2% cutoff" in their legends.

For simplicity and consistency, numerical abundance data were presented in terms of actual numbers of individuals collected, rather than as extrapolated values. For example, to convert density to numbers per metre square, it is necessary to multiply the count per station-period (i.e. six grabs) by 1.66. Sediment texture parameters were depicted graphically using the triangles of Buchanan and Kain (1971).

4.3 Results

LGL identified 267 taxa of macroinfaunal invertebrates in the 1979 and 1980 samples (Table 4-3). The numbers of taxa identified at all 12 stations taken together showed major changes from one sampling period to the next (Figure 4-3). Statistically significant differences ($P \leq 0.05$) in numbers of taxa identified separated the 1979 and 1980 sampling periods

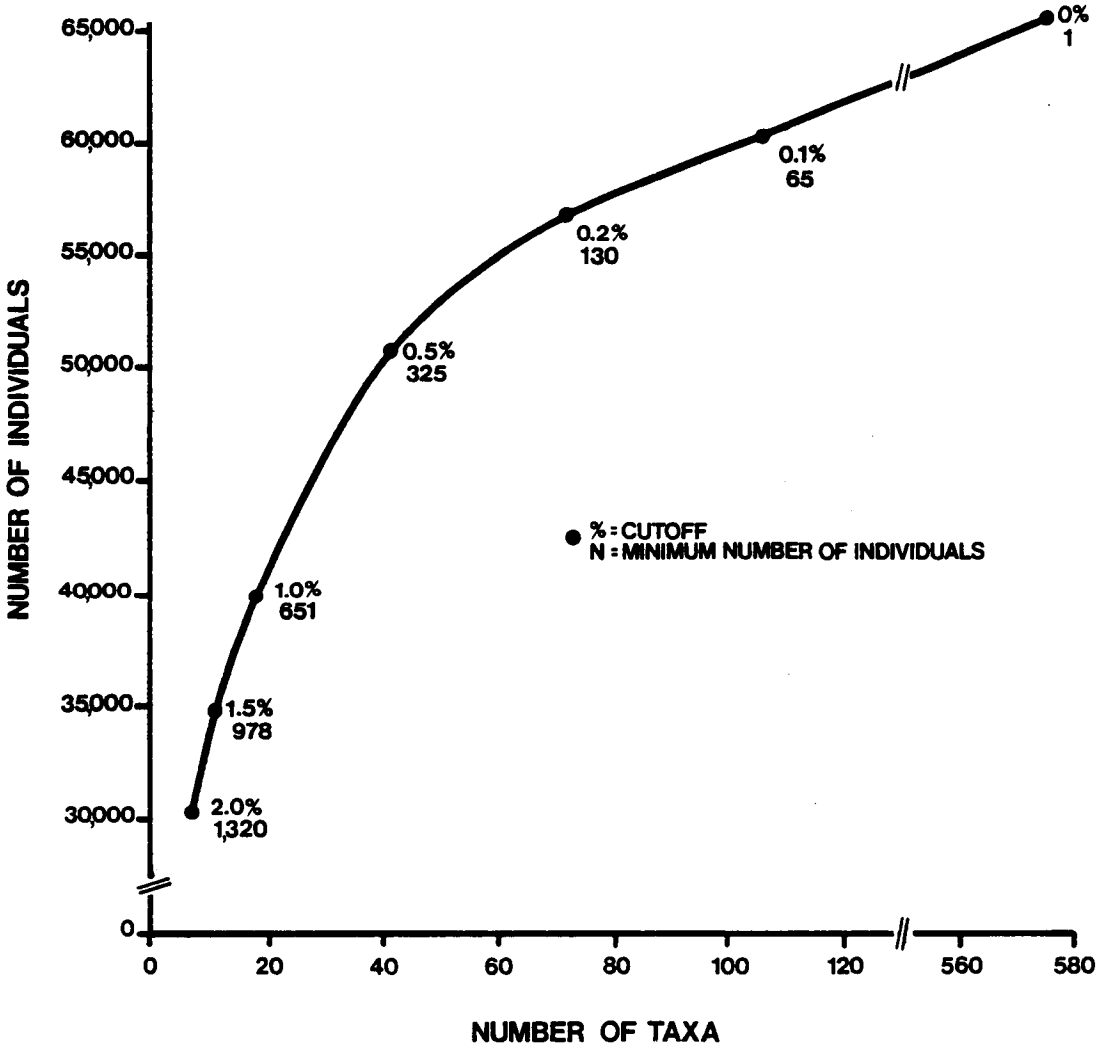


Figure 4-2. Total individuals and numbers of taxa remaining at various minimum cutoff values.

Table 4-3. Taxonomic checklist for 1979 and 1980 LGL samples. Equivalent University of Texas (STOCS) names are in parentheses.

PHYLUM CNIDARIA
- CLASS Hydrozoa
  - Suborder Gymnoblastea
    - Tubularidae
      - *Ectopleura grandis* (*Tubularia* sp.—UT)
  - Suborder Calyptoblastea
    - Campanulinidae
      - *Calycella syringa*
      - *Lovenella grandis*
- CLASS Anthozoa
  - Miscellaneous octocoral polyps (unid.)
  - Order Gorgonacea
    - *Leptogorgia setacea* (gorgonian, unid.—UT)
  - Order Pennatulacea
    - *Virgularia mirabilis* (sea pen, unid.—UT)
    - Renillidae
      - *Renilla mulleri*
  - Order Zoanthidea
    - *Palythoa texaensis*
    - Miscellaneous zoantharians (unid.)
  - Order Actiniaria
    - Actiniarian sp. A
    - Miscellaneous anemones (unid.)
  - Order Ceriantharia
    - Ceriantharian (unid.)

PHYLUM NEMERTINEA
- Miscellaneous nemerteans (unid.)

PHYLUM NEMATODA
- Miscellaneous nematodes (unid.)

PHYLUM ECTOPROCTA
- *Bugula* sp. (Bryozoans, unid.—UT)

PHYLUM PHORONIDA
- Miscellaneous phoronids (unid.)

PHYLUM BRACHIOPODA
- Lingulidae
  - *Glottidia pyramidata*

PHYLUM MOLLUSCA
- CLASS Gastropoda
  - Vitrinellidae
    - *Cyclostremiscus pentagonus*
    - *Vitrinella floridana*
  - Melanellidae
    - *Liostraca bilineata*
  - Aclididae
    - *Bermudaclis* sp.

Table 4-3 (cont'd)

- Naticidae
  - *Natica pusilla*
  - *Polynices duplicatus*
  - *Sinum maculatum*
  - *Sinum perspectivum*
- Columbellidae
  - *Anachis avara*
  - *Anachis obesa*
  - *Anachis pulchella*
- Buccinidae
  - *Cantharus cancellaria*
- Nassariidae
  - *Nassarius acutus*
- Olividae
  - *Oliva sayana*
  - *Olivella dealbata*
- Turridae
  - *Kurtziella cerinella*
- Terebridae
  - *Terebra protexta*
- Pyramidellidae
  - *Odostomia acutidens*
  - *Pyramidella crenulata*
  - *Turbonilla interrupta*
- Cylichnidae
  - *Cylichnella bidentata*
- Retusidae
  - *Volvulella persimilis*
  - *Volvulella texasiana*
- Aglajidae
  - *Aglaja* sp. nov.

Order Nudibranchia

- Corambidae
  - *Doridella obscura*

CLASS Scaphopoda

- Siphonodentaliidae
  - *Cadulus carolinensis*
- Dentaliidae
  - *Dentalium eboreum*
  - *Dentalium texasianum*

CLASS Pelecypoda

- Nuculidae
  - *Nucula aegeensis*
- Nuculanidae
  - *Nuculana acuta*
  - *Nuculana concentrica*
- Arcidae
  - *Anadara ovalis*
  - *Anadara transversa*
  - *Arcopsis adamsi*
- Lucinidae
  - *Lucina amiantus*
  - *Parvilucina multilineata*

Table 4-3 (cont'd)

Ungulinidae
Diplodonta cf. *punctata*
Cardiidae
Laevicardium laevigatum
Tellinidae
Macoma tenta
Macoma sp.
Tellina aequistriata
Tellina sybaritica
Tellina versicolor
Semelidae
Abra aequalis
Veneridae
Chione clenchi
Chione grus
Dosinia discus
Pitar cordatus
Petricolidae
Petricola pholadiformis
Corbulidae
Corbula caribaea
Corbula dietziana
Corbula sp.
Varicorbula disparilis
Gastrochaenidae
Gastrochaena hians
Periplomatidae
Periploma inequale

PHYLUM ANNELIDA
CLASS Polychaeta
Polynoidae
Eunoe nodulosa
Lepidasthenia maculata
Eulepethidae
Grubeulepis mexicana
Polyodontidae
Polyodontes lupina
Eupanthalis kinbergi
Sigalionidae
Sthenelais limicola
Thalanessa sp. A
Palmyridae
Bhawania goodei
Amphinomidae
Linopherus ambigua
Phyllodocidae
Eteone lactea
Phyllodoce mucosa

Table 4-3 (cont'd)

Pilargiidae
- Ancistrosyllis commensalis
- Ancistrosyllis jonesi
- Cabira incerta
- Litocorsa stremma
- Pilargis berkelyae
- Sigambra bassi
- Sigambra tentaculata
- Sigambra wassi

Hesionidae
- Gyptis brevipalpa

Syllidae
- Exogone dispar
- Exogone verugera

Nereidae
- Ceratocephale sp.
- Ceratonereis irritabilis
- Nereis cf. grayii
- Nereis lamellosa
- Nereis micromma (Nereidae [Nicon] sp. A--UT)
- Nereis succinea
- Nereis sp. D

Nephtyidae
- Aglaophamus verrilli
- Nephtys incisa
- Nephtys picta

Glyceridae
- Glycera americana
- Glycera sp. A

Goniadidae
- Goniada littorea
- Ophioglycera sp.
- Ophioglycera sp. A

Eunicidae
- Marphysa sp. A

Onuphidae
- Diopatra cuprea
- Onuphis cf. quadricuspis
- Onuphis sp. A
- Onuphis sp. B
- Onuphis sp. C

Lumbrineridae
- Lumbrineris cruzensis (L. cf. magalhaensis--UT)
- Lumbrineris ernesti (L. tenuis--UT)
- Lumbrineris januarii
- Lumbrineris sp. nov. (L. parvepedata--UT)
- Ninoe nigripes

Arabellidae
- Arabella iricolor
- Drilonereis magna

Dorvilleidae
- Schistomeringos rudolphi

Table 4-3 (cont'd)

Spionidae
- *Apoprionospio pygmaea*
- *Laonice cirrata*
- *Malacoceros* sp.
- *Paraprionospio pinnata*
- *Prionospio cirrobranchiata* (*Minuspio cirrifera*--UT)
- *Prionospio cristata*
- *Prionospio steenstrupi*
- *Scolelepis* sp.
- *Spiophanes bombyx*

Magelonidae
- *Magelona cincta*
- *Magelona longicornis*
- *Magelona pettiboneae*
- *Magelona phyllisae*
- *Magelona* cf. *sacculata*

Chaetopteridae
- *Spiochaetopterus costarum oculatus*

Cirratulidae
- *Chaetozone corona* (*C. setosa*--UT)
- *Tharyx marioni*
- *Tharyx setigera*
- *Tharyx* sp.

Heterospionidae
- *Heterospio longissima*

Cossuridae
- *Cossura delta*

Orbiniidae
- *Haploscoloplos foliosus*
- *Haploscoloplos fragilis*
- *Scoloplos rubra*

Paraonidae
- *Aricidea finitima*
- *Aricidea fragilis*
- *Aricidea taylori*
- *Aricidea* sp.
- *Paraonides lyra*
- *Paraonis gracilis*

Opheliidae
- *Armandia agilis*
- *Armandia maculata*

Capitellidae
- *Capitella capitata*
- *Mediomastus californiensis*
- *Notomastus hemipodus*
- *Notomastus* cf. *latericeus*

Maldanidae
- *Asychis carolinae*
- *Clymenella torquata*
- *Proclymene* sp.

Oweniidae
- *Owenia fusiformis*

Table 4-3 (cont'd)

Sabellaridae
Sabellaria vulgaris vulgaris
Pectinariidae
Pectinaria gouldii
Ampharetidae
Ampharete acutifrons
Ampharete parvidentata
Isolda pulchella
Melinna maculata
Terebellidae
Loimia viridis
Pista quadrilobata
Polycirrus cf. *carolinensis*
Trichobranchidae
Terebellides stroemii
Sabellidae
Chone filicaudata

PHYLUM SIPUNCULA
Phascolion sp.
Miscellaneous sipunculids (unid.)

PHYLUM ARTHROPODA
CLASS Crustacea
SUBCLASS Ostracoda
Miscellaneous ostracods (unid.)
SUBCLASS Malacostraca
Order Mysidacea
Anchialina typica
Bowmaniella brasiliensis
Bowmaniella floridana
Bowmaniella cf. *portoricensis*
Metamysidopsis swifti
Mysidopsis bigelowi
Order Cumacea
Cyclaspis pustulata
Cyclaspis varians
Cyclaspis sp. B
Eudorella monodon
Oxyurostylis sp.
Order Tanaidacea
Apseudes sp. A
Kalliapseudes sp.
Typhlapseudes sp.
Order Isopoda
Anthuridae
Xenanthura brevitelson
Idoteidae
Edotea montosa
Erichsonella attenuata
Sphaeromatidae
Ancinus depressus

Table 4-3 (cont'd)

Order Stomatopoda
- *Squilla empusa*
- *Squilla neglecta*

Order Amphipoda

Caprellidae
- *Paracaprella pusilla*

Ampeliscidae
- *Ampelisca abdita*
- *Ampelisca agassizi*
- *Ampelisca verrilli*
- *Ampelisca* sp. B
- *Ampelisca* sp.

Melitidae
- *Eriopsia* sp. B

Oedicerotidae
- *Monoculodes nyei* (*Monoculodes* sp. B--UT)
- *Synchelidium americanum*

Corophiidae
- *Cerapus* sp.
- *Erichthonius brasiliensis*
- *Grandidierella* sp.
- *Neomegamphopus* sp.
- *Photis melanicus* (*Photis* sp. B--UT)
- *Unciola serrata*

Lysianassidae
- *Hippomedon* cf. *serratus*

Bateidae
- *Batea* sp.

Synopiidae
- *Tiron tropakis*

Liljeborgiidae
- *Listriella barnardi*
- *Listriella* sp. A

Phoxocephalidae
- *Trichophoxus floridanus* (*Paraphoxus epistomus*--UT)

Haustoriidae
- *Acanthohaustorius millsi*
- *Platyischnopus* sp.
- *Protohaustorius bousfieldi*

Stenothoidae
- *Parametopella texensis*

Amphilochidae
- Amphilochid sp. A

Order Decapoda

Penaeidae
- *Penaeus* sp.
- *Trachypenaeus constrictus*
- *Trachypenaeus* sp.
- *Xiphopenaeus kroyeri*

Sicyoniidae
- *Sicyonia dorsalis*

Sergestidae
- *Acetes americanus*

Table 4-3 (cont'd)

Pasiphaeidae
Leptochela serratorbita
Palaemonidae
Pontonia sp.
Alpheidae
Alpheus sp. A
Alpheus sp. B
Automate sp.
Hippolytidae
Latreutes parvulus
Ogyrididae
Ogyrides limicola
Processidae
Processa sp.
Callianassidae
Callianassa biformis
Upogebiidae
Upogebia affinis
Porcellanidae
Porcellana sayana
Paguridae
Pagurus cf. *bullisi*
Albuneidae
Albunea gibbesi
Albunea paretii
Calappidae
Hepatus epheliticus
Osachila sp.
Leucosiidae
Persephona crinita
Persephona mediterranea
Majidae
Libinia emarginata
Portunidae
Portunus gibbesii
Xanthidae
Hexapanopeus angustifrons
Goneplacidae
Chasmocarcinus mississippiensis
Frevillea barbata
Glyptoplax smithi
Speocarcinus lobatus
Speocarcinus sp.
Pinnotheridae
Pinnixa cf. *retinens*
Pinnixa sp.

PHYLUM ECHINODERMATA
CLASS Ophiuroidea
Amphiuridae
Amphiura stimpsoni
Micropholis atra

Table 4-3 (cont'd)

Ophiactidae
Hemipholis elongata

CLASS Echinoidea
Order Clypeasteroida
Melitidae
Mellita quinquiesperforata
Order Spatangoida
Schizasteridae
Moira atropos
CLASS Holothuroidea
Order Dendrochirotida
Cucumariidae
Pentamera pulcherrima
Thione mexicana
Order Apodida
Synaptidae
Protankyra cf. *benedeni*
Order Molpadiida
Holothuriidae
Holothuria cubana

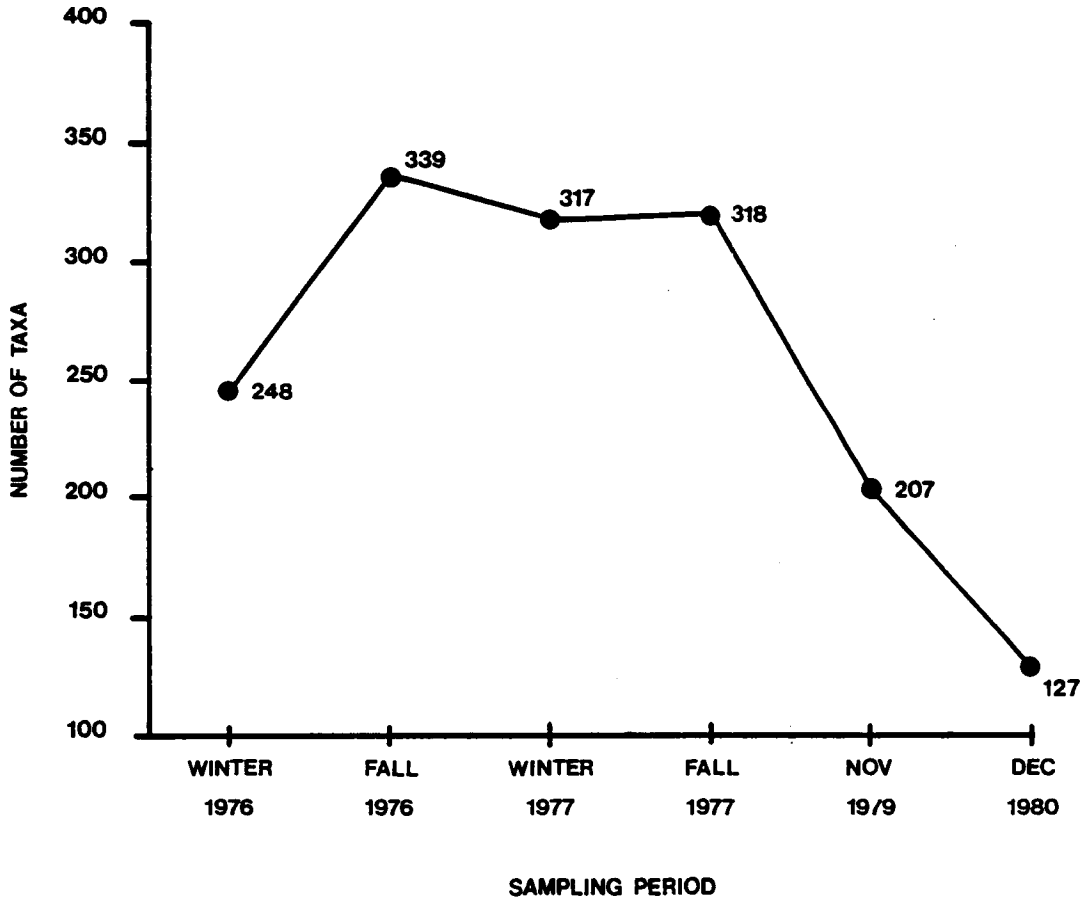


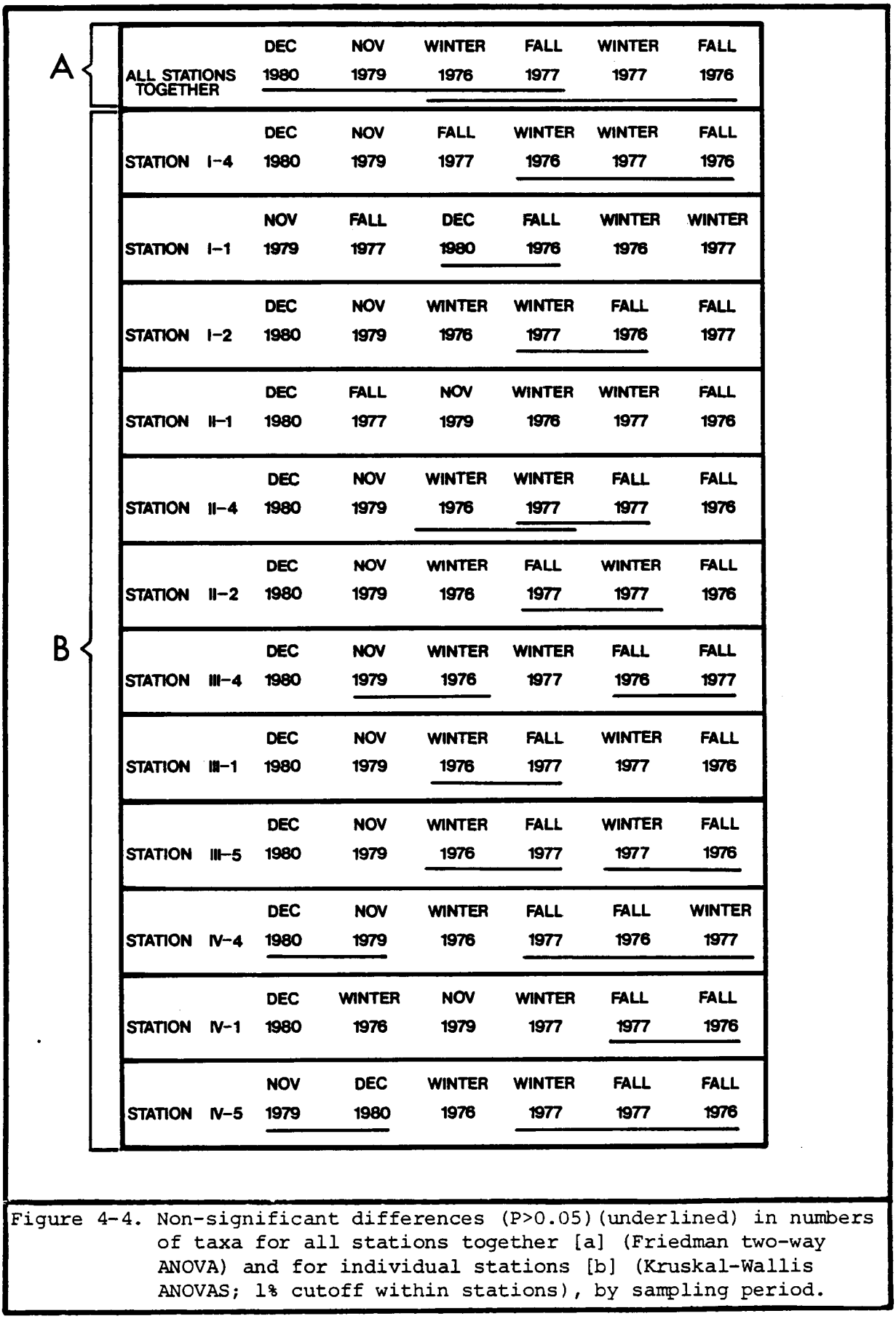
Figure 4-3. Number of taxa at all stations together, by sampling period.

from the fall 1976 and winter 1977 sampling periods, with winter 1976 and fall 1977 sampling periods falling between the two pairs (Figure 4-4A). Winter 1976, 1979 and 1980 samples included fewer taxa than did the other three sampling periods. Many taxa were present in more than 1 sampling period (Figure 4-5), although most were collected only once (201 taxa) or twice (116 taxa). There were many significant differences in numbers of macroinfaunal taxa identified from one sampling period to the next, within stations (Figure 4-4B).

The numbers of individuals of macroinfaunal taxa collected at all 12 stations taken together changed sharply from one sampling period to the next (Figure 4-6). Many of the less common taxa were extremely rare. For example, 105 taxa (18% of the total 576 taxa included in this study) were represented by only one individual; five or fewer individuals were collected for 249 taxa (43% of 576). The 1979 and 1980 samples included fewer individuals than did any of the other sampling periods. The Friedman two-way ANOVA for all stations together by sampling period (Figure 4-7A) highlighted a distinct break in abundance, with 1979 and 1980 samples having relatively low numbers of individuals, and winter and fall 1977 sampling periods having relatively high numbers of individuals. The two sets of time periods differed significantly, sharing one sampling period (winter 1976) with intermediate abundance between the two. Within stations, there were also many statistically significant differences from one time period to the next in the abundance of numerically dominant taxa (Figure 4-7B).

The strongest associations between sampling periods in terms of numbers of taxa identified (based on numbers of non-significant ($P > 0.05$) pairs in the Kruskal-Wallis ANOVA) were those between the three sampling periods having highest numbers of identified taxa: fall 1976, winter 1977, and fall 1977 (four pairs each). This may be seen in Figure 4-8, a derivative of Figures 4-4 and 4-7, in which the numbers within each shaded square equal the number of times two time periods were connected by an unbroken line (i.e. a non-significant difference) in Figure 4-4B or 4-7B (top and bottom, respectively, of Figure 4-8). Other less frequent pairings included winter 1976 with winter 1977, winter 1976 with fall 1977, and 1979 with 1980 (two pairs each). The strongest associations between sampling periods in terms of numbers of individuals were between fall 1977 and winter 1977, and fall 1976 and winter 1977 (five pairs each). Other less strong associations were between winter 1976 and winter 1977 (four pairs); fall 1976 and fall 1977, and 1979 and 1980 (three pairs each); and between winter 1976 and fall 1976, winter 1976 and fall 1977, winter 1976 and 1979, and winter 1976 and 1980 (two pairs each).

When all stations were grouped together, the relative proportions of numbers of individuals of each numerically dominant taxon (Figure 4-9) remained fairly constant. The polychaetes Magelona phyllisae (Magelonidae), Lumbrineris sp. nov. (Lumbrineridae), and Paraprionospio pinnata (Spionidae); and miscellaneous unidentified sipunculids and nemerteans were consistent components through time. The relative proportions of each major group of taxa (Figure 4-10) for all stations together also were rather stable. Deposit feeding and carnivorous or



A	ALL STATIONS TOGETHER	DEC 1980	NOV 1979	WINTER 1976	FALL 1977	WINTER 1977	FALL 1976
B	STATION I-4	DEC 1980	NOV 1979	FALL 1977	WINTER 1976	WINTER 1977	FALL 1976
	STATION I-1	NOV 1979	FALL 1977	DEC 1980	FALL 1976	WINTER 1976	WINTER 1977
	STATION I-2	DEC 1980	NOV 1979	WINTER 1976	WINTER 1977	FALL 1976	FALL 1977
	STATION II-1	DEC 1980	FALL 1977	NOV 1979	WINTER 1976	WINTER 1977	FALL 1976
	STATION II-4	DEC 1980	NOV 1979	WINTER 1976	WINTER 1977	FALL 1977	FALL 1976
	STATION II-2	DEC 1980	NOV 1979	WINTER 1976	FALL 1977	WINTER 1977	FALL 1976
	STATION III-4	DEC 1980	NOV 1979	WINTER 1976	WINTER 1977	FALL 1976	FALL 1977
	STATION III-1	DEC 1980	NOV 1979	WINTER 1976	FALL 1977	WINTER 1977	FALL 1976
	STATION III-5	DEC 1980	NOV 1979	WINTER 1976	FALL 1977	WINTER 1977	FALL 1976
	STATION IV-4	DEC 1980	NOV 1979	WINTER 1976	FALL 1977	FALL 1976	WINTER 1977
	STATION IV-1	DEC 1980	WINTER 1976	NOV 1979	WINTER 1977	FALL 1977	FALL 1976
	STATION IV-5	NOV 1979	DEC 1980	WINTER 1976	WINTER 1977	FALL 1977	FALL 1976

Figure 4-4. Non-significant differences (P>0.05)(underlined) in numbers of taxa for all stations together [a] (Friedman two-way ANOVA) and for individual stations [b] (Kruskal-Wallis ANOVAS; 1% cutoff within stations), by sampling period.

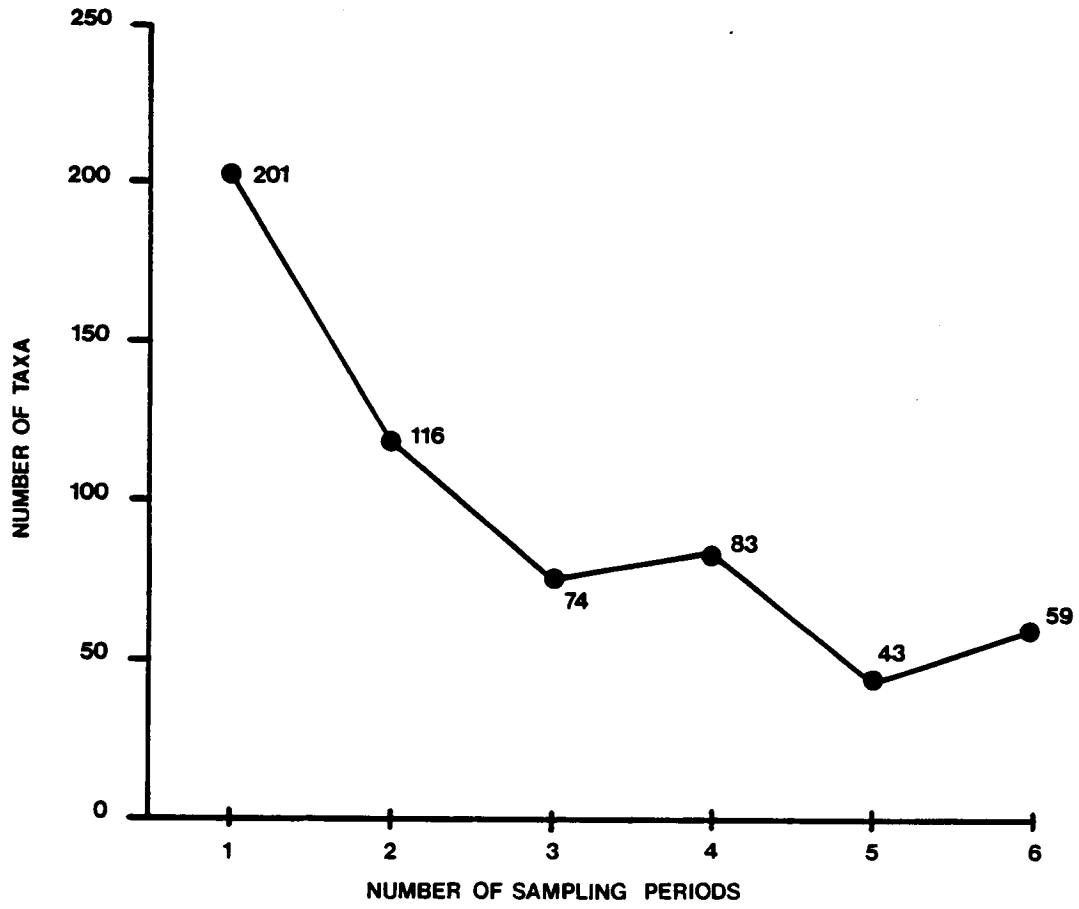


Figure 4-5. Number of taxa occurring in one or more sampling periods.

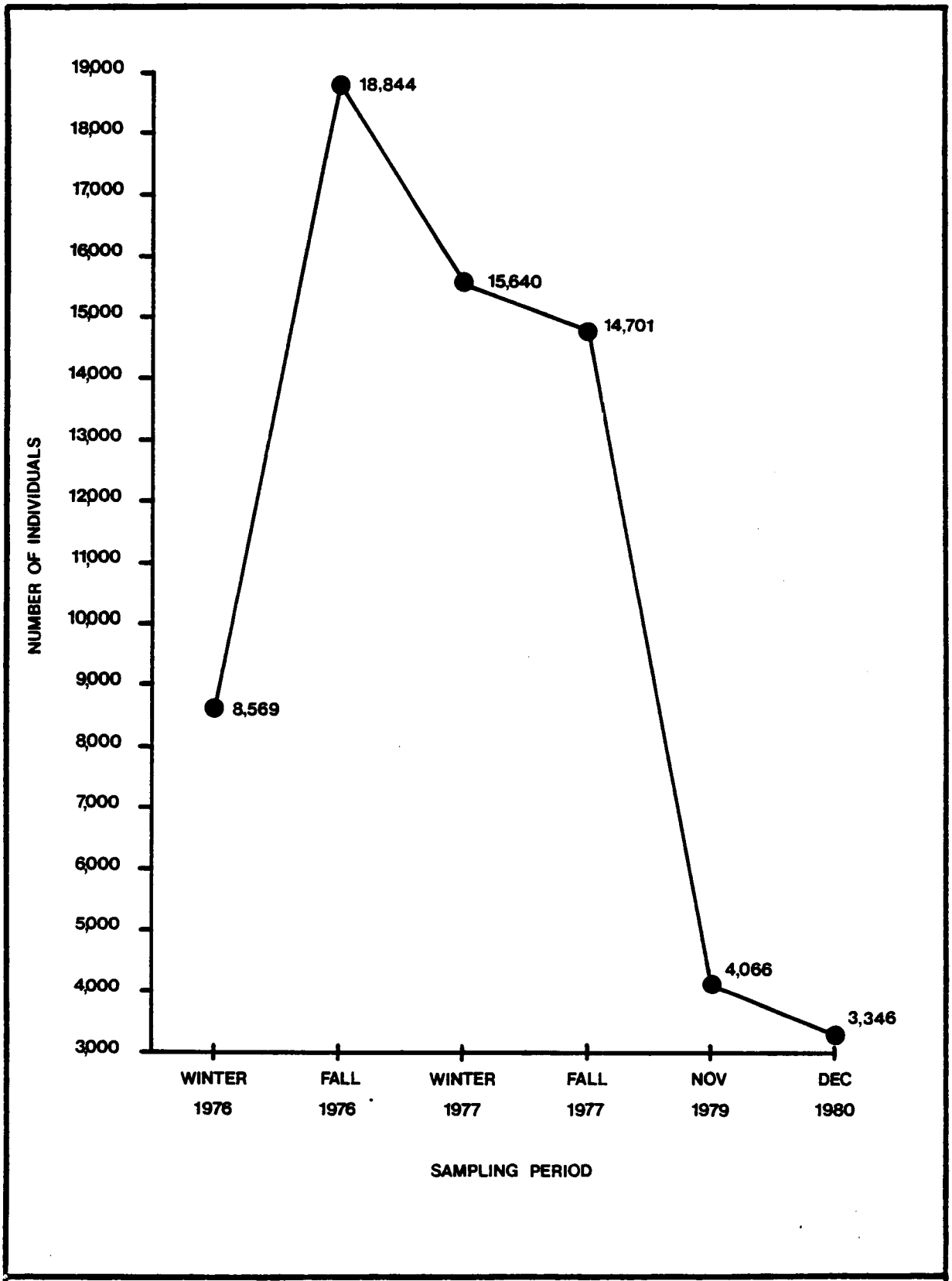


Figure 4-6. Number of individuals at all stations together (six 0.1 m^2 grabs/station x 12 stations = 7.2 m^2) by sampling period.

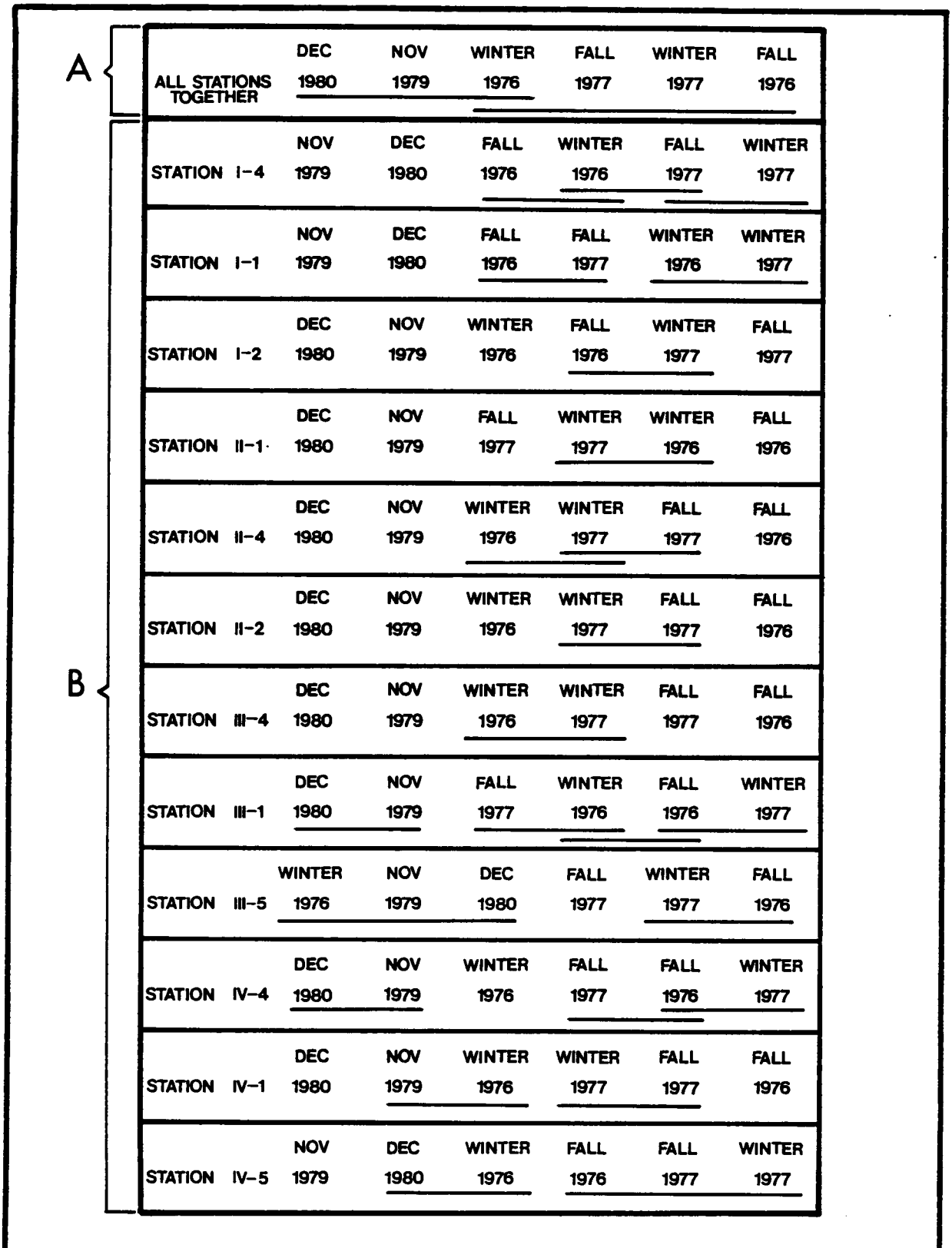


Figure 4-7. Non-significant differences (P>0.05)(underlined) in numbers of individuals for all stations together [A](Friedman two-way ANOVA); and for individual stations [B](Kruskal-Wallis ANOVAS; 1% cutoff within stations), by sampling period.

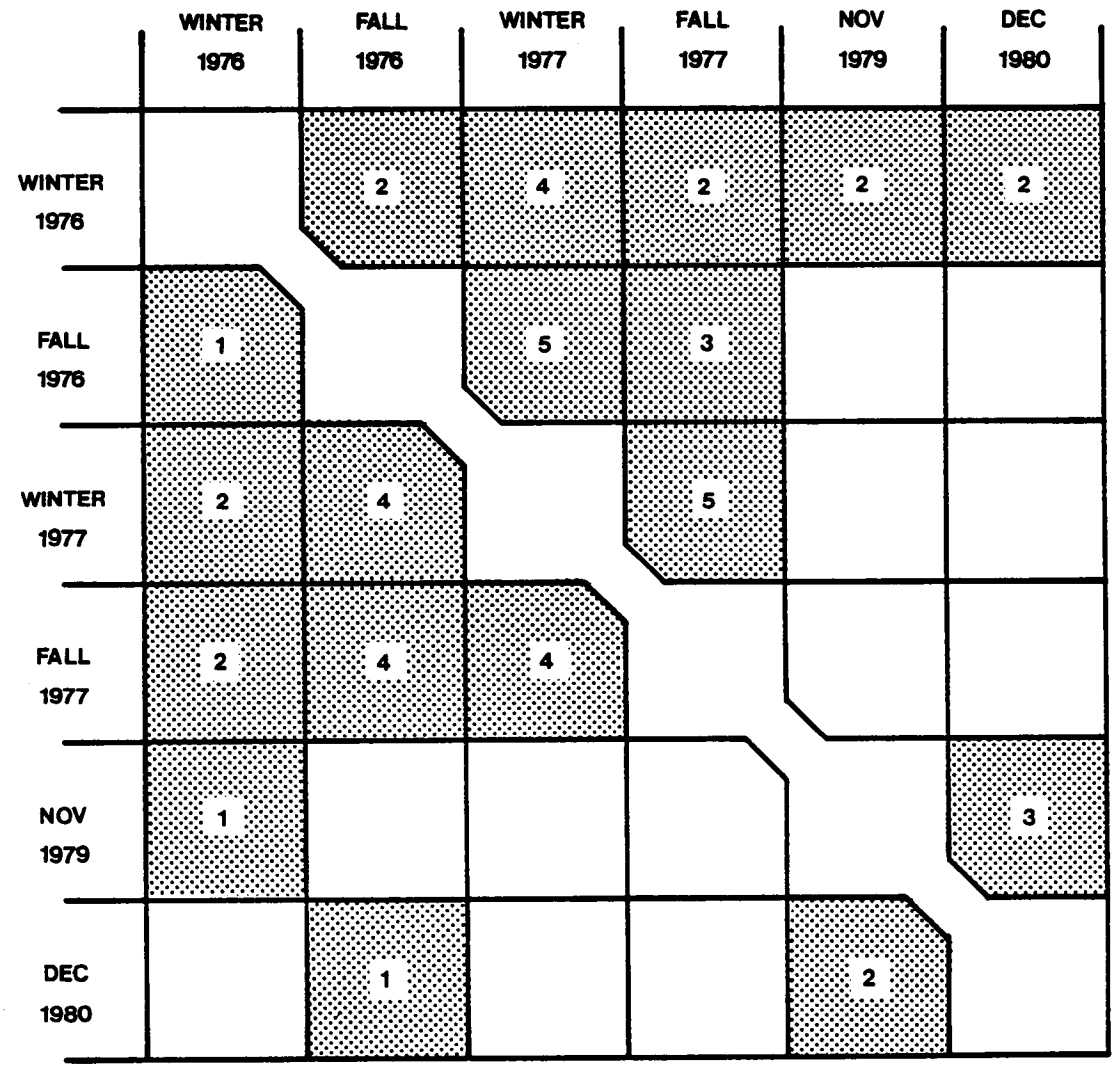


Figure 4-8. Associations between sampling periods for numbers of individuals (top) and numbers of taxa (bottom), based on total non-significant (P>0.05) pairs between time periods (numbers within shaded areas) in the Kruskal-Wallis ANOVAS (1% cutoff within stations); see text for explanation.

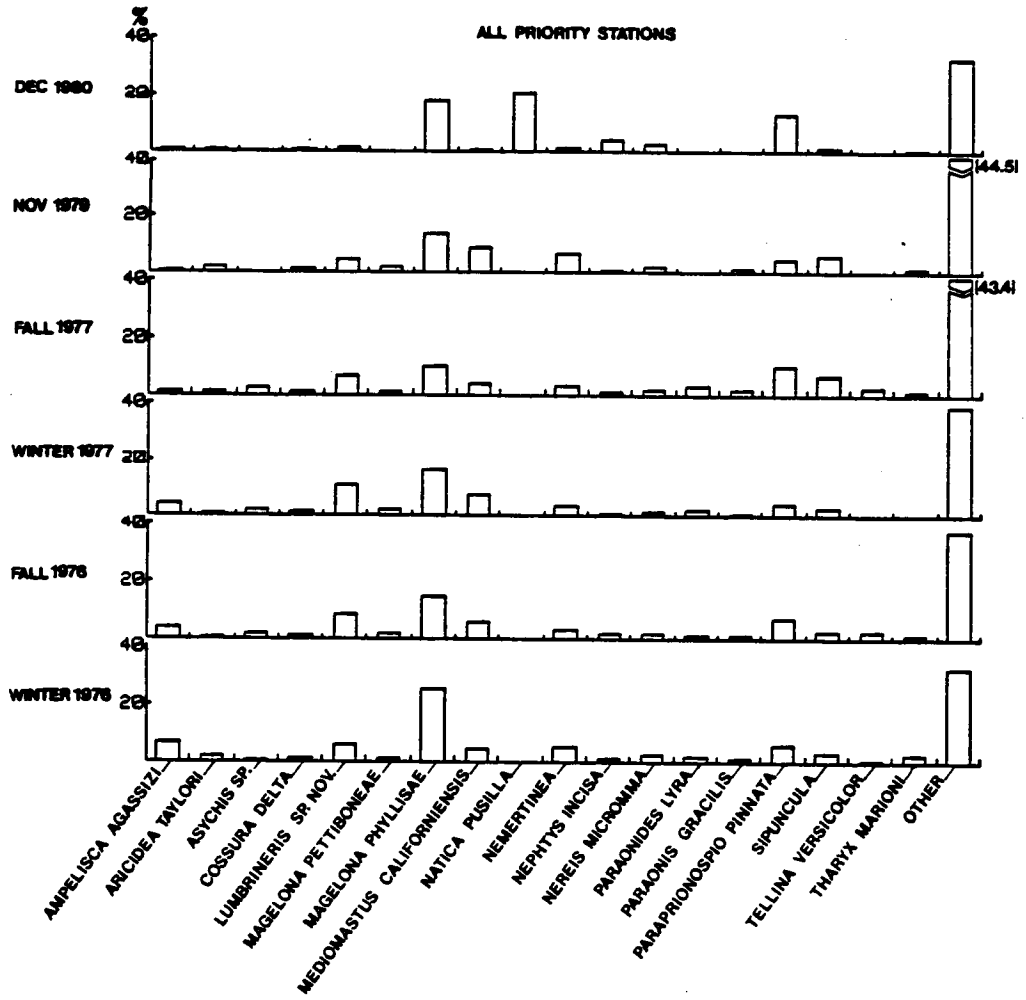


Figure 4-9. Relative proportions of numbers of individuals of numerically dominant taxa for all stations together, by sampling period (1% cutoff).

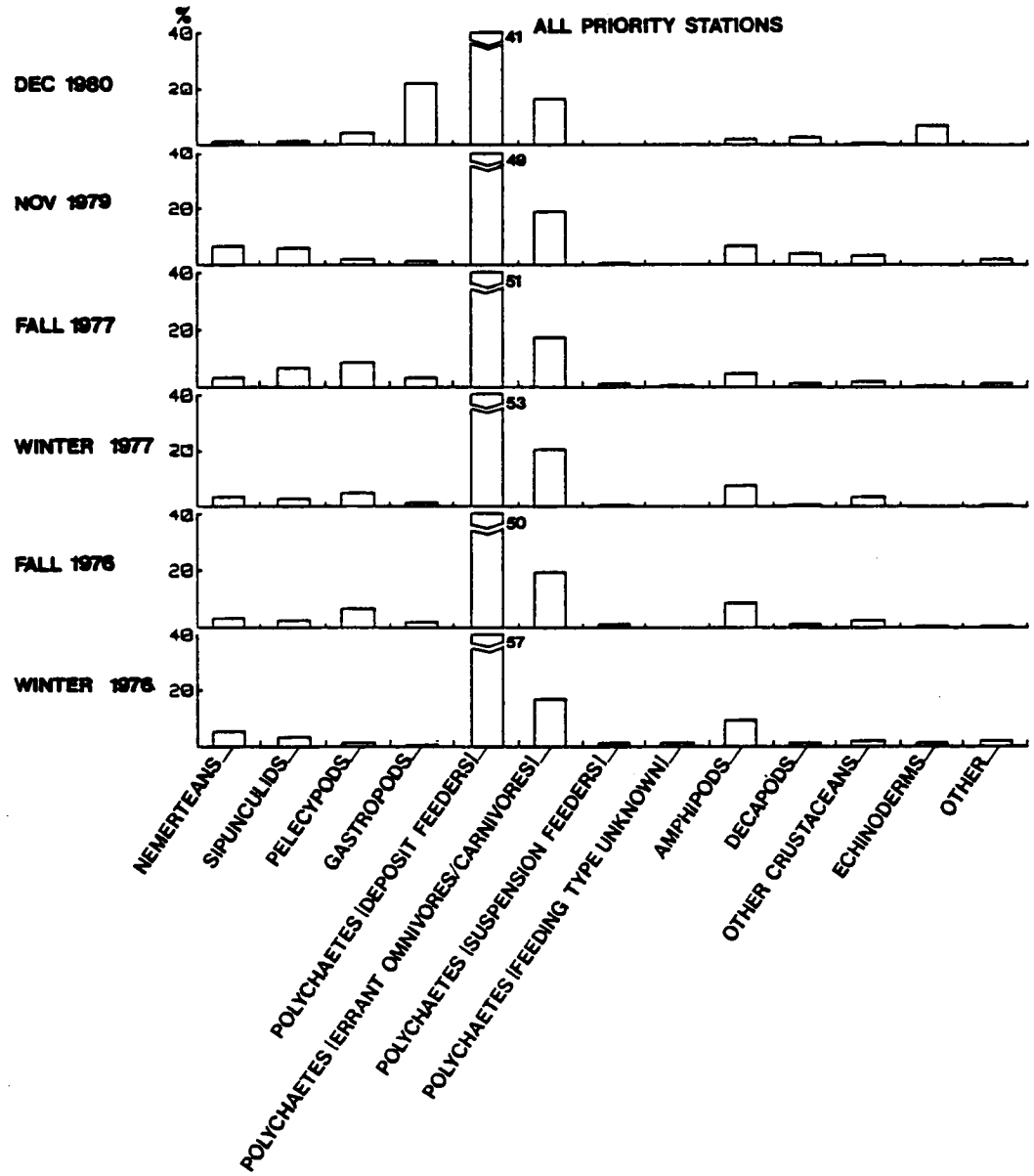


Figure 4-10. Relative proportions of numbers of individuals of major groups of taxa for all stations together, by sampling period.

omnivorous polychaetes were most important, followed by amphipods, molluscs, sipunculids, and nemerteans. However, large fluctuations in the abundance of any given taxon and even of the major groups of taxa were common at most stations from one time period to the next (Figures 4-11 through 4-34).

Diversity (H') for all taxa together showed its highest values during fall 1977 (4.13), fall 1976 (3.97), and 1979 (3.95). Winter 1977, winter 1976, and 1980 values were 3.86, 3.55, and 3.14 respectively, viewing all stations together (Figure 4-35). Evenness (V') was highest in 1979 (0.74) and fall 1977 (0.70). Fall 1976, winter 1977, winter 1976, and 1980 showed lower values (0.67, 0.66, 0.63, and 0.62 respectively). On a station-by-station basis, changes in numbers of taxa and individuals were accompanied by a variety of responses of H' and V', ranging from simultaneous increases or decreases in both indices, to increases or decreases in one or the other index without a concordant change in the other (Figures 4-36 through 4-47, Table 4-4). A test for internal consistency was performed on both indices to confirm that they were acting on the data set in the manner for which they were designed. The test results supported the use of the indices, showing that H' was positively correlated with numbers of taxa (sign test $p = 0.01$) but was independent of changes in overall numbers of individuals, and that V' was neither correlated with numbers of individuals nor with numbers of taxa.

When numerically abundant taxa were grouped into two presence/absence association diagrams, one focusing upon station groupings with depth and the other upon sampling periods (Figures 4-48 and 4-49 respectively), a number of trends were revealed. The taxa listed in both diagrams are presented in order of increasing average depth of collection (top to bottom).

Figure 4-48 is divided into six individual rectangular grids, one per sampling period. The horizontal scale within each sampling period lists stations by increasing depth (left to right). Thus, taxa present (+) primarily at shallow stations appear at the upper left of each of the six rectangular grids, while those present primarily at deeper stations appear toward the bottom right of each grid.

Figure 4-49 displays presence/absence data grouped into twelve rectangular grids, each of which represents a single station. Stations are ordered by increasing depth (left to right). The horizontal scale within each station lists sampling periods in chronological sequence, from winter 1976 ("1") through 1980 ("6"). Thus, taxa that were common at shallower stations appear toward the left side of Figure 4-49, while those common at deeper stations appear toward the right side. Taxa most frequently found in deeper water appear toward the bottom of the figure, while those restricted to shallow water appear toward the top of the figure.

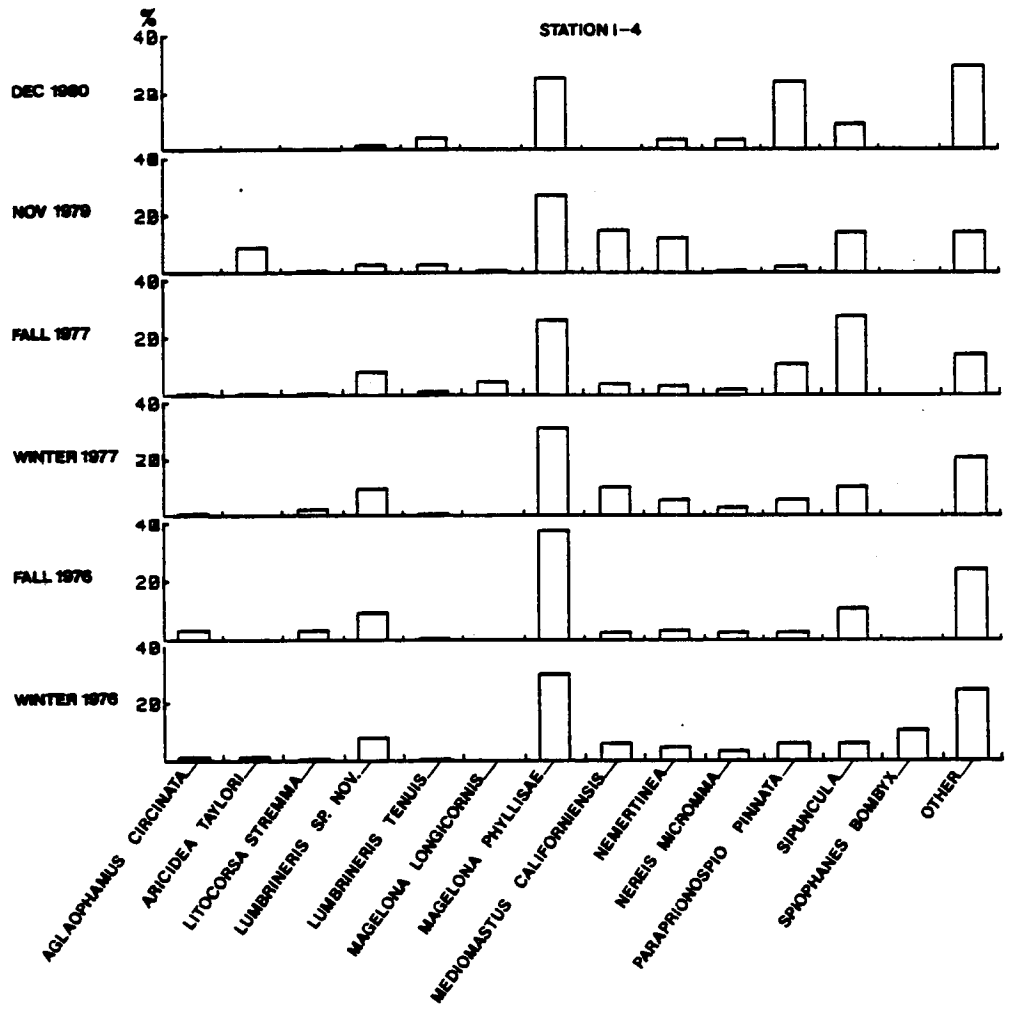


Figure 4-11. Relative proportions of numbers of individuals of numerically dominant taxa at Station I-4 (1% cutoff).

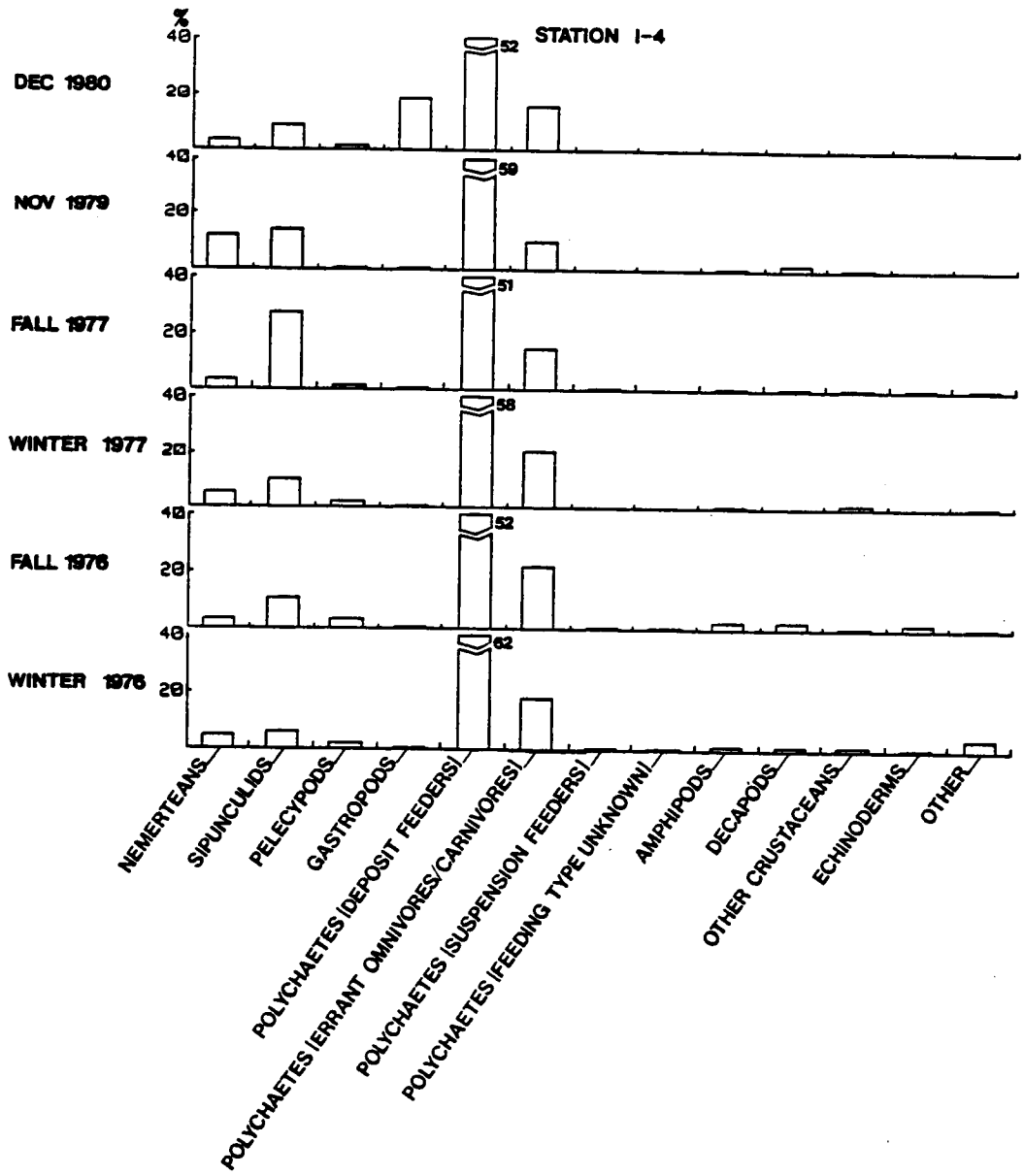


Figure 4-12. Relative proportions of numbers of major groups of numerically dominant taxa at Station I-4, by sampling period (1% cutoff).

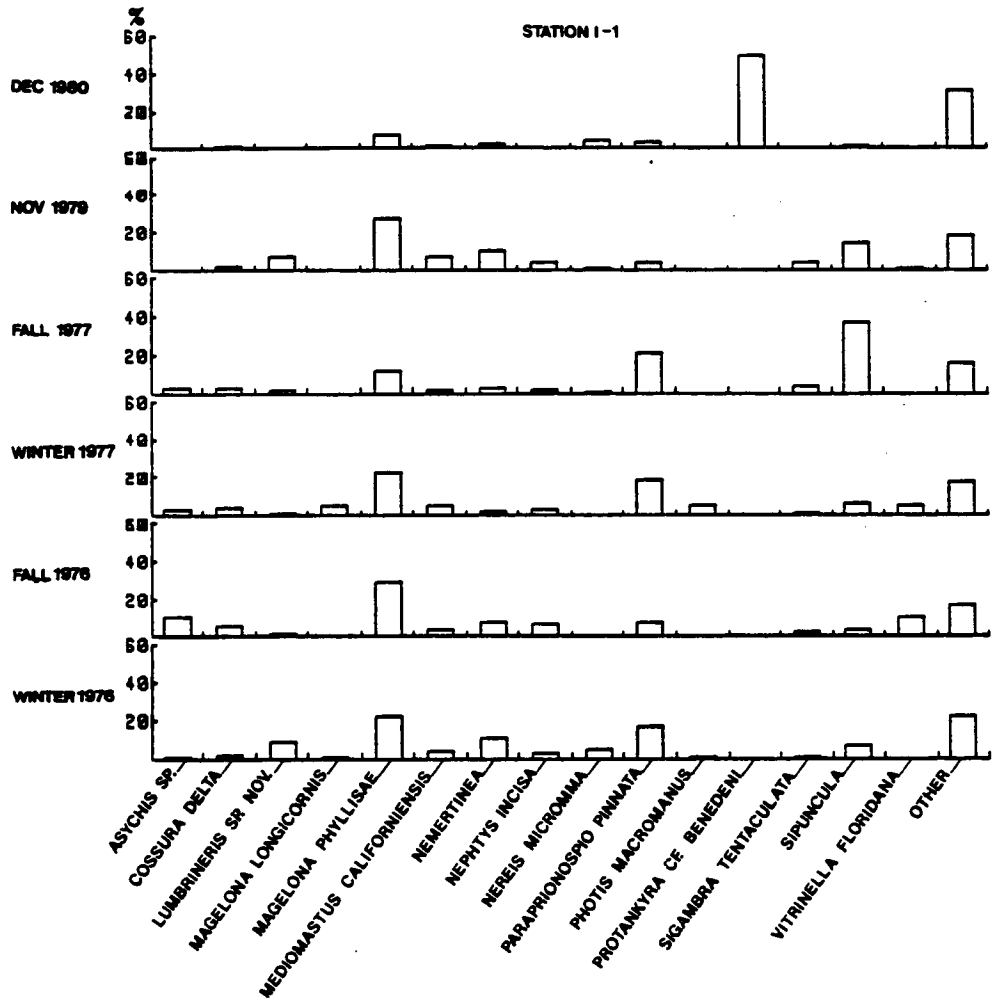


Figure 4-13. Relative proportions of numbers of individuals of numerically dominant taxa at Station I-1, by sampling period (1% cutoff).

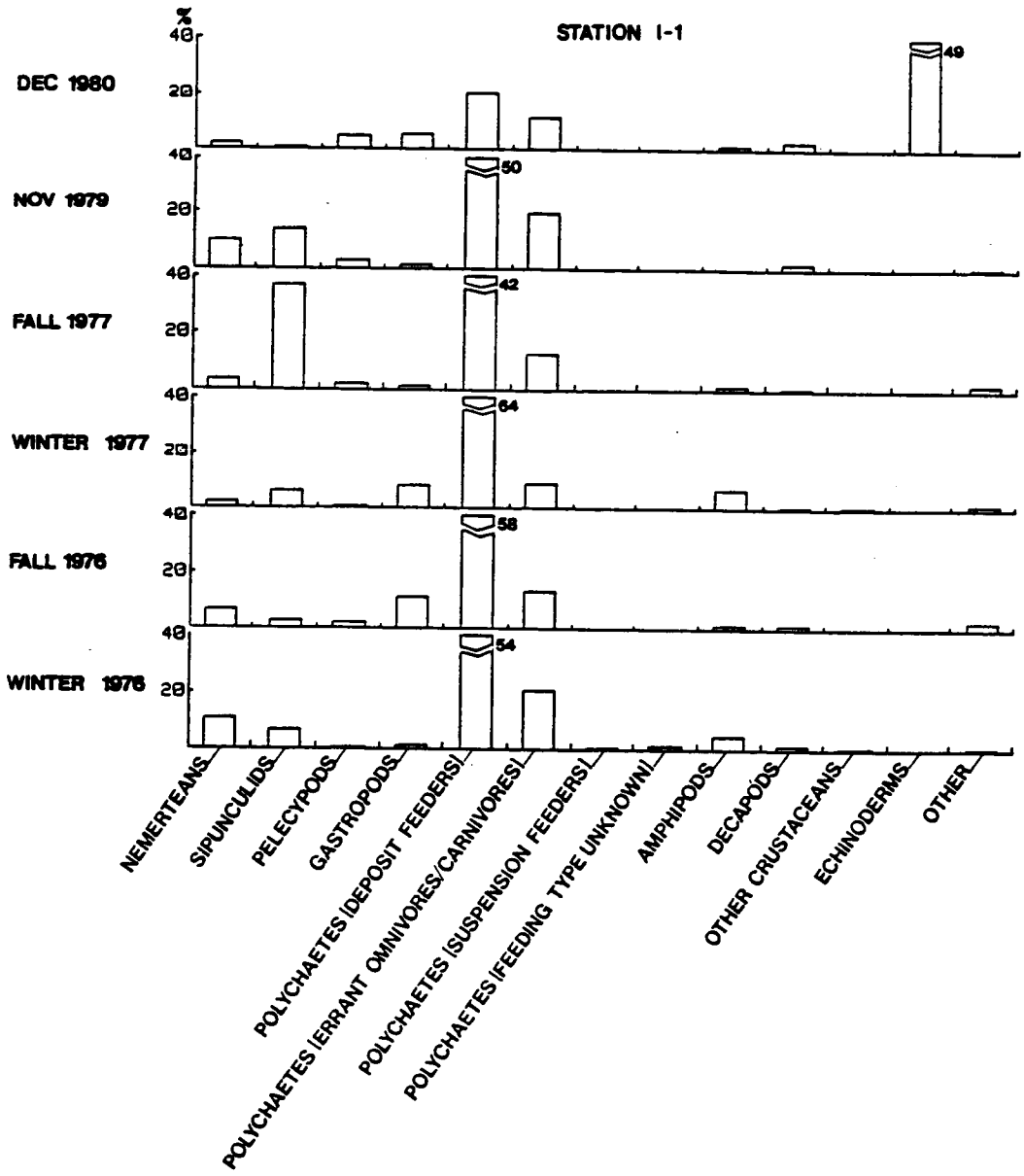


Figure 4-14. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station I-1, by sampling period (1% cutoff).

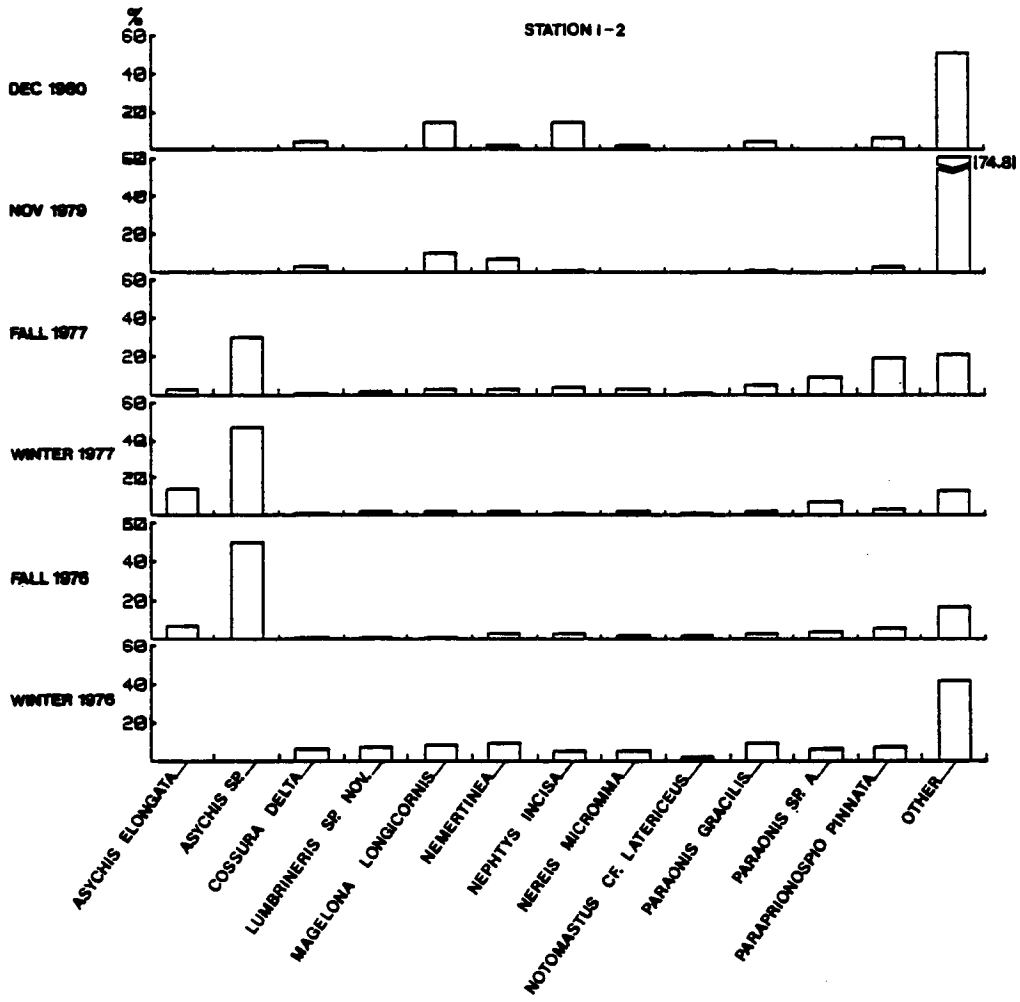


Figure 4-15. Relative proportions of numbers of individuals of numerically dominant taxa at Station I-2, by sampling period (1% cutoff).

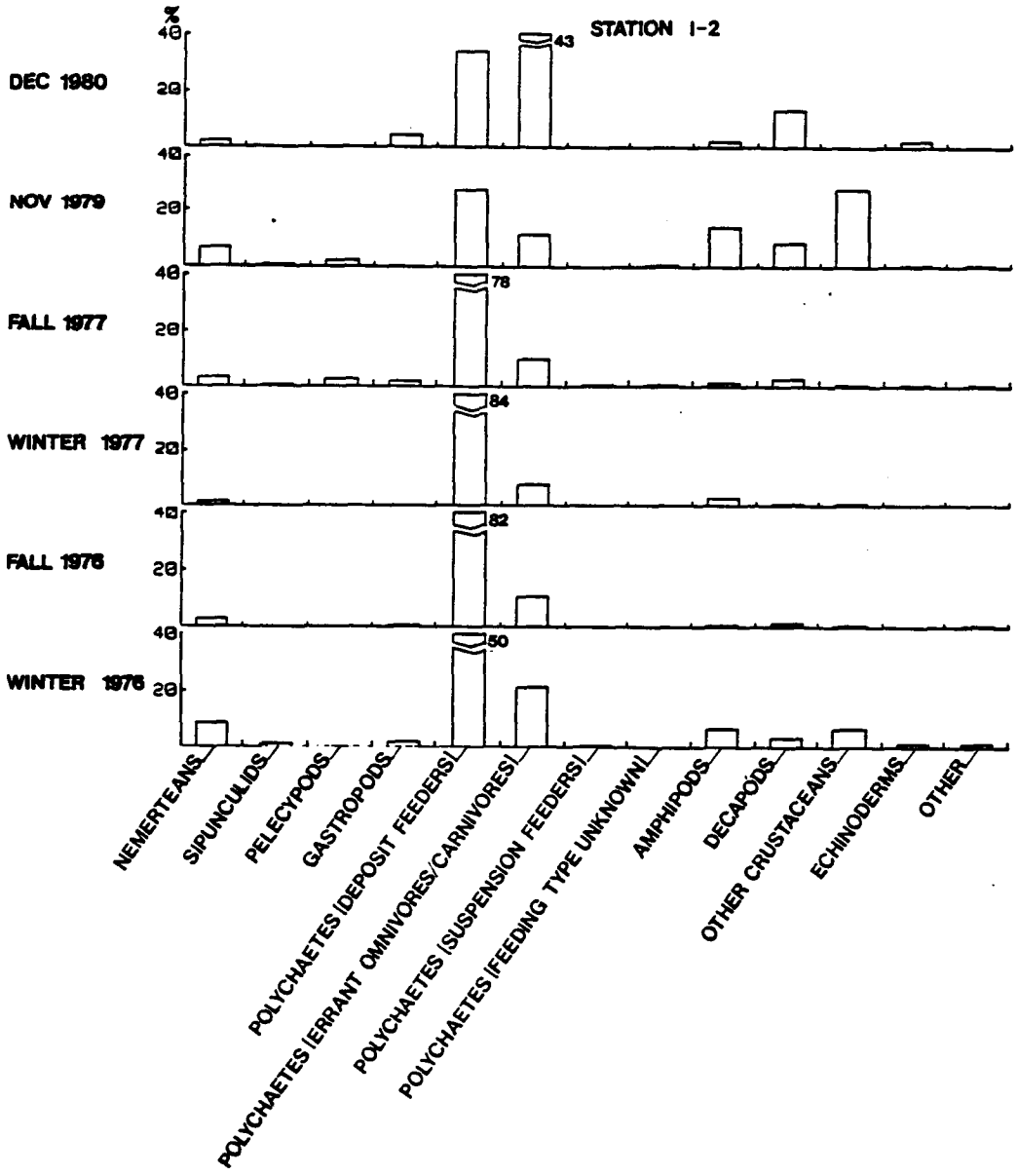


Figure 4-16. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station I-2, by sampling period (1% cutoff).

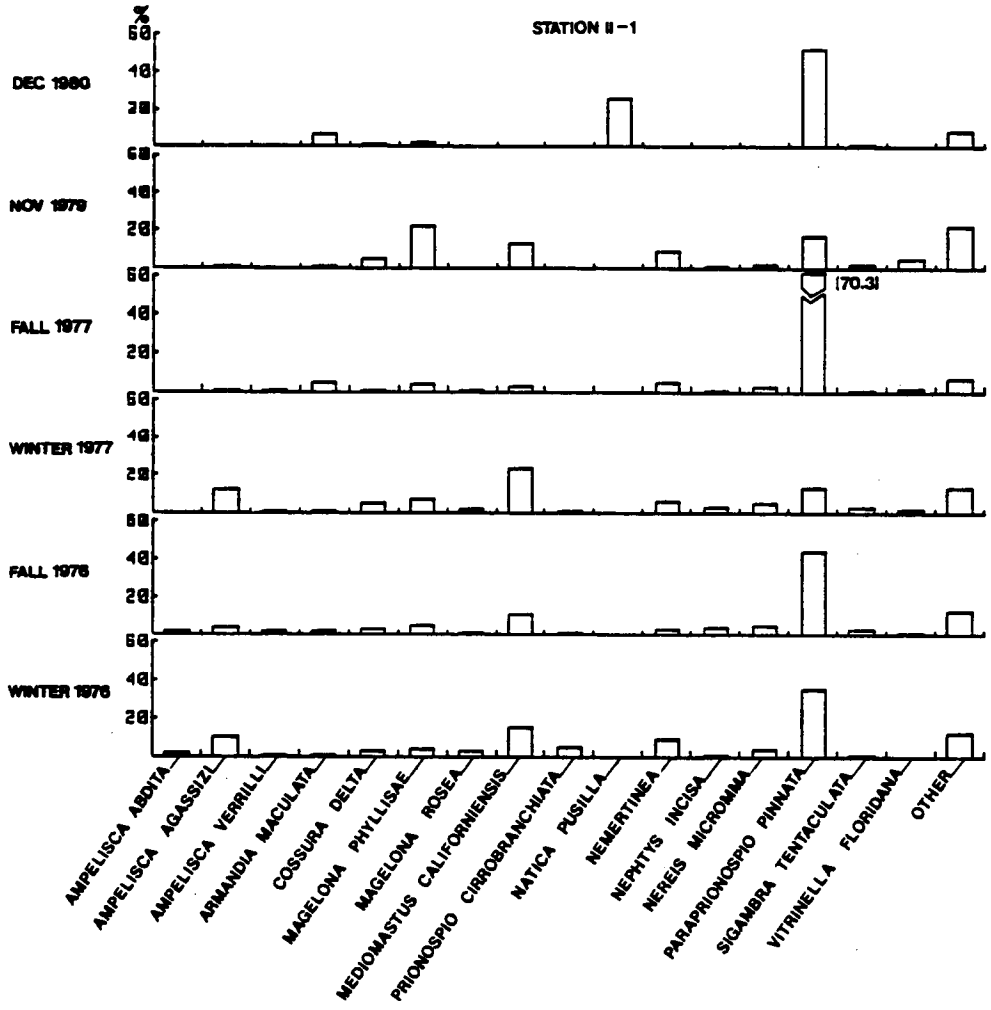


Figure 4-17. Relative proportions of numbers of individuals of numerically dominant taxa at Station II-1, by sampling period (1% cutoff).

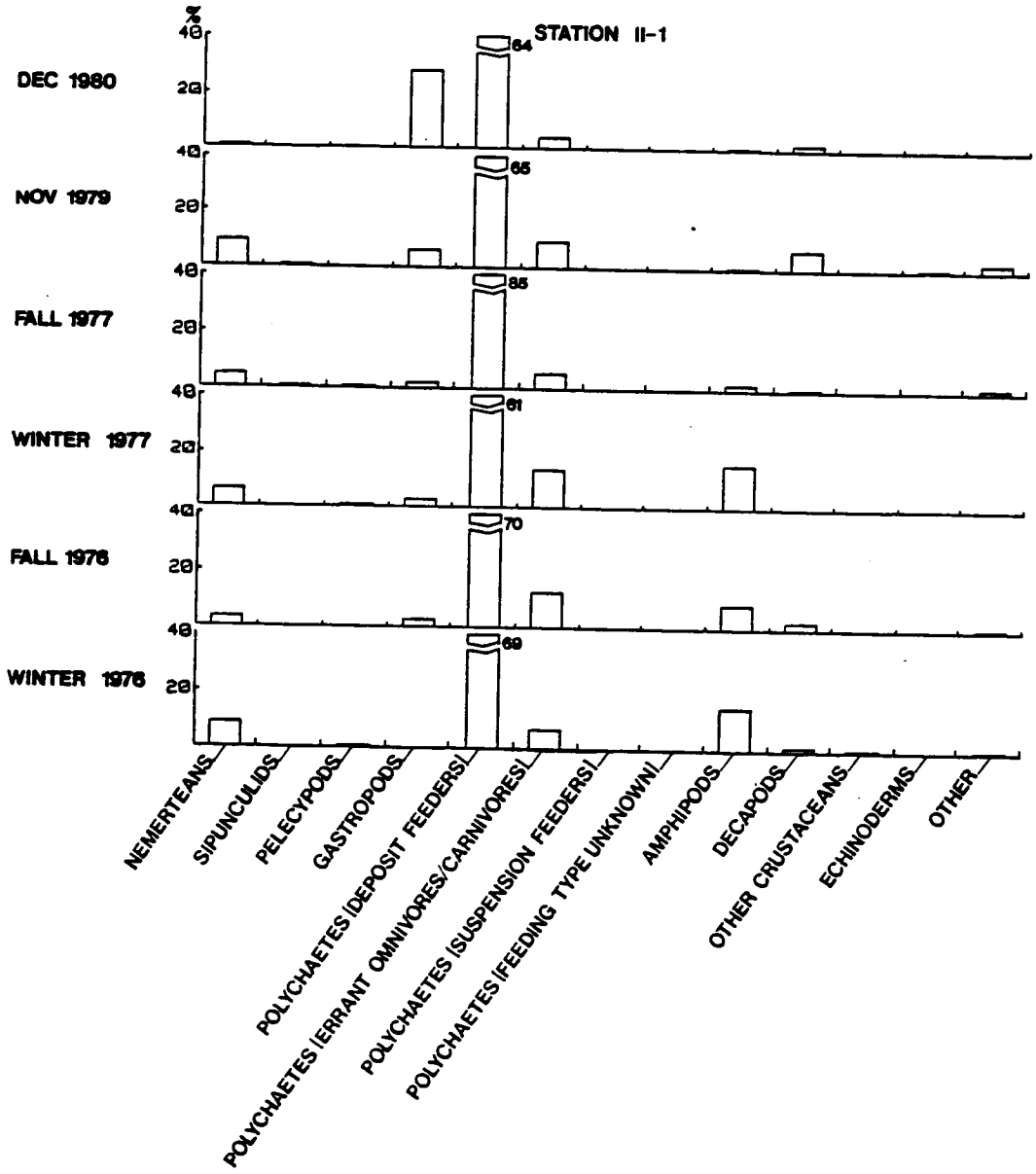


Figure 4-18. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station II-1, by sampling period (1% cutoff).

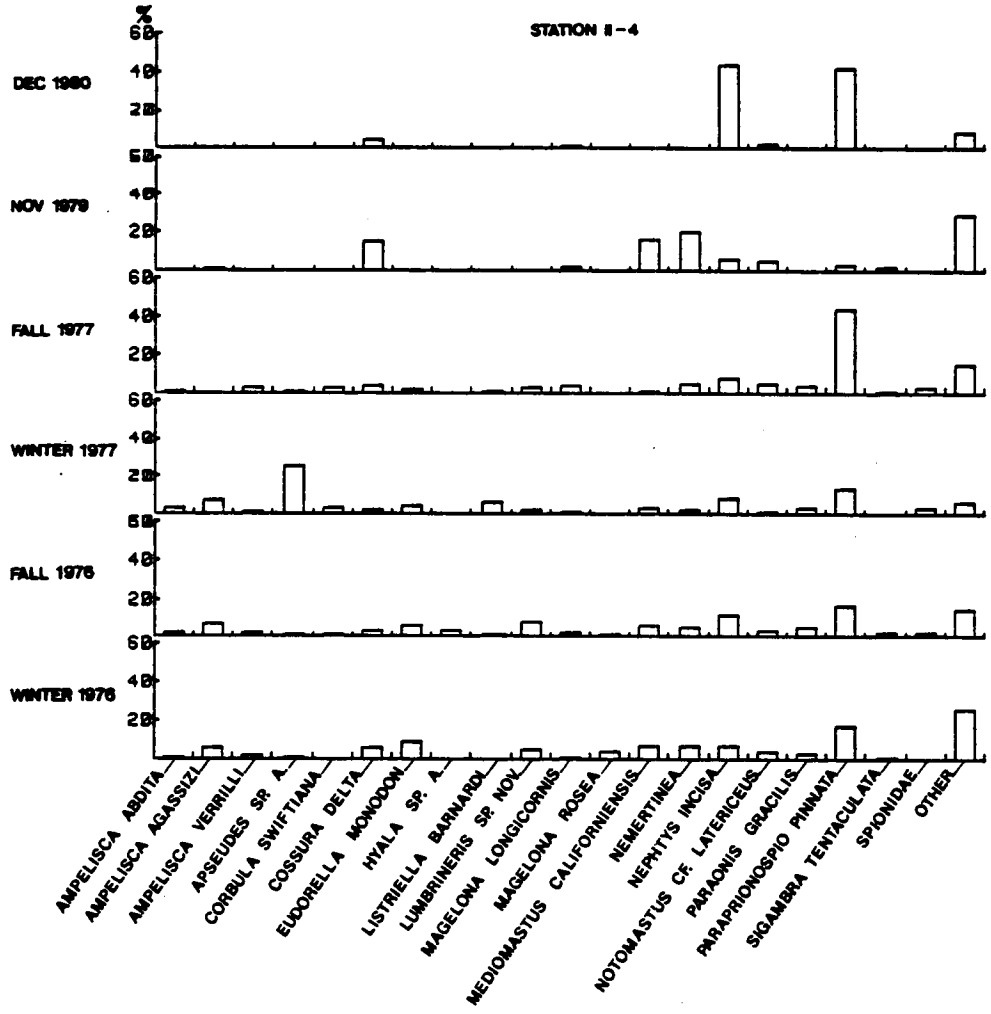


Figure 4-19. Relative proportions of numbers of individuals of numerically dominant taxa at Station II-4, by sampling period (1% cutoff).

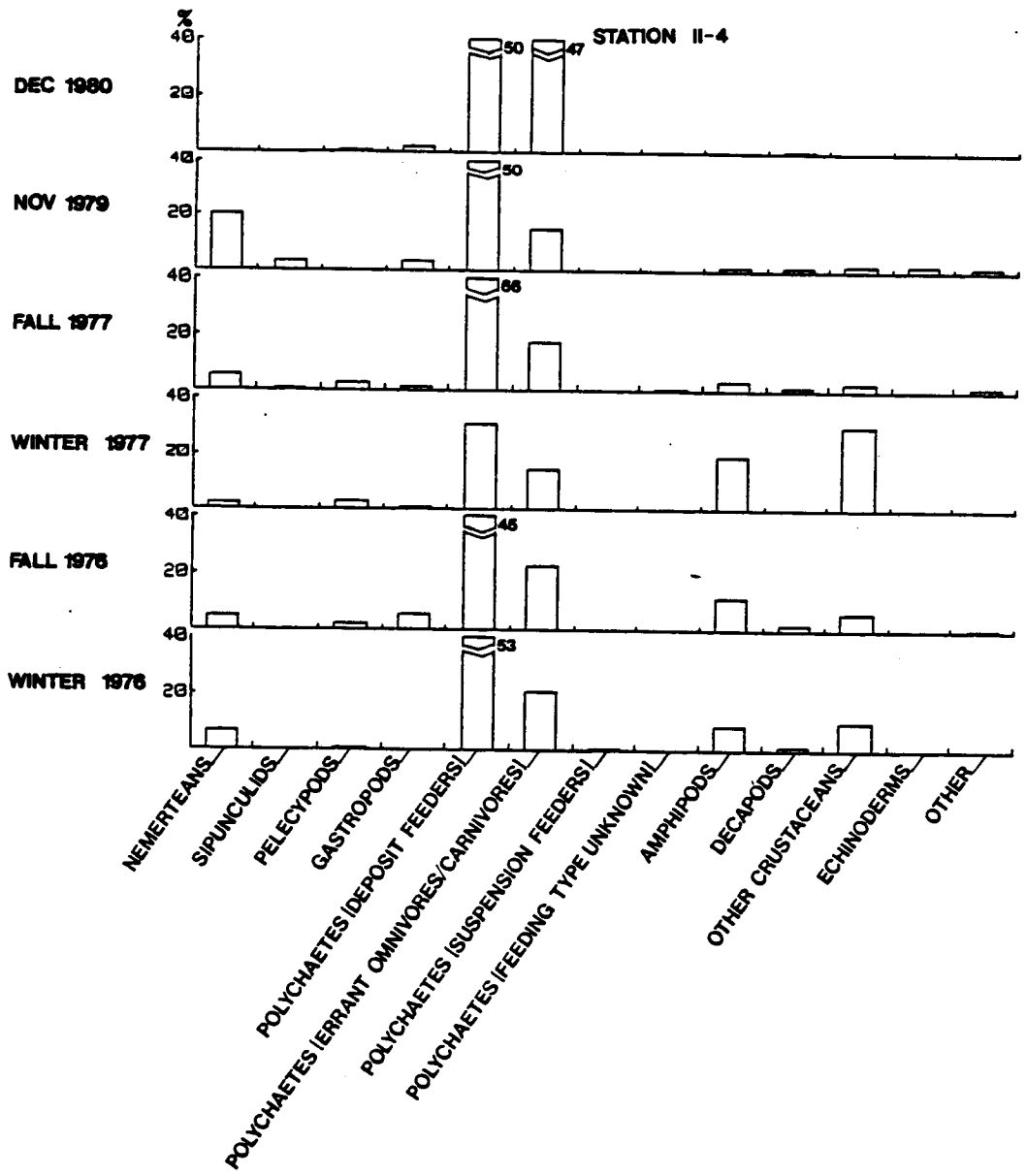


Figure 4-20. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station II-4, by sampling period (1% cutoff).

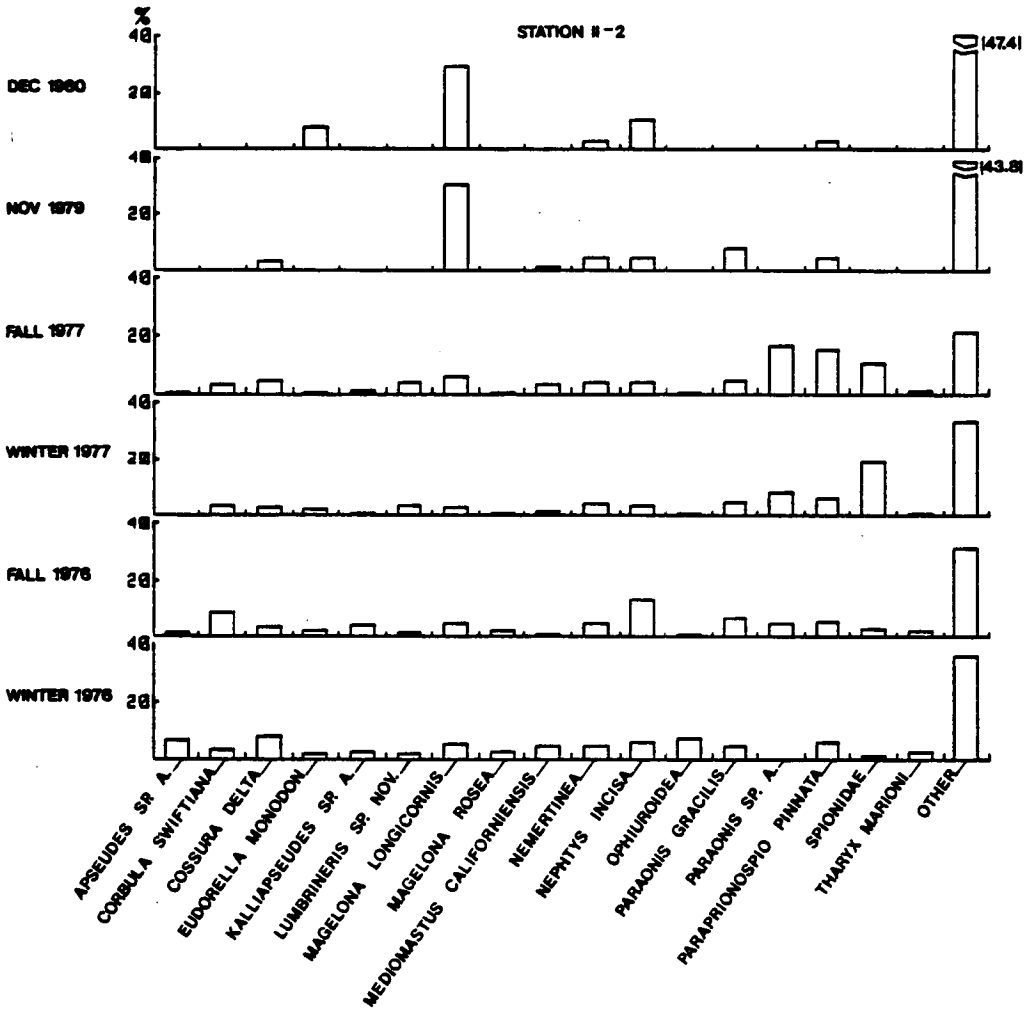


Figure 4-21. Relative proportions of numbers of individuals of numerically dominant taxa at Station II-2, by sampling period (1% cutoff).

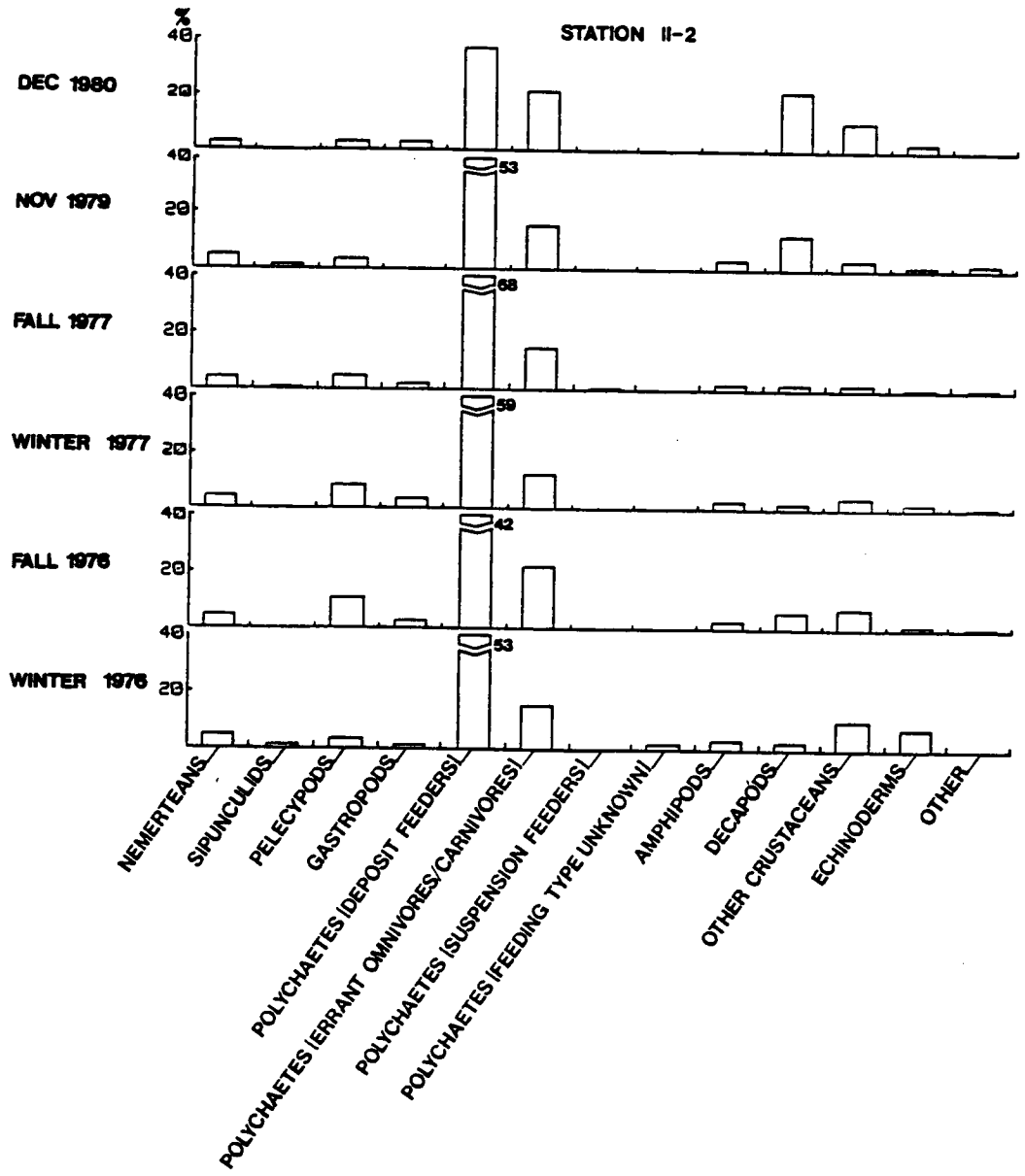


Figure 4-22. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station II-2, by sampling period (1% cutoff).

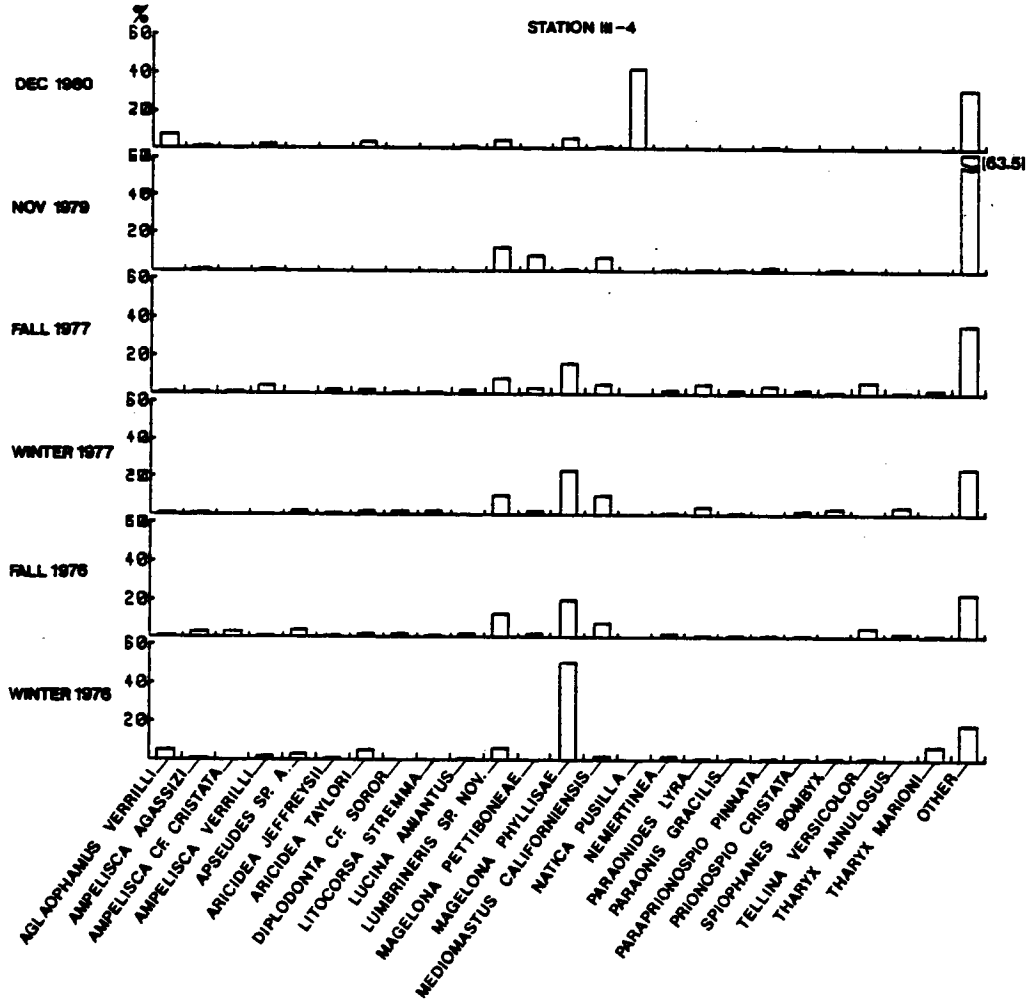


Figure 4-23. Relative proportions of numbers of individuals of numerically dominant taxa at Station III-4, by sampling period (1% cutoff).

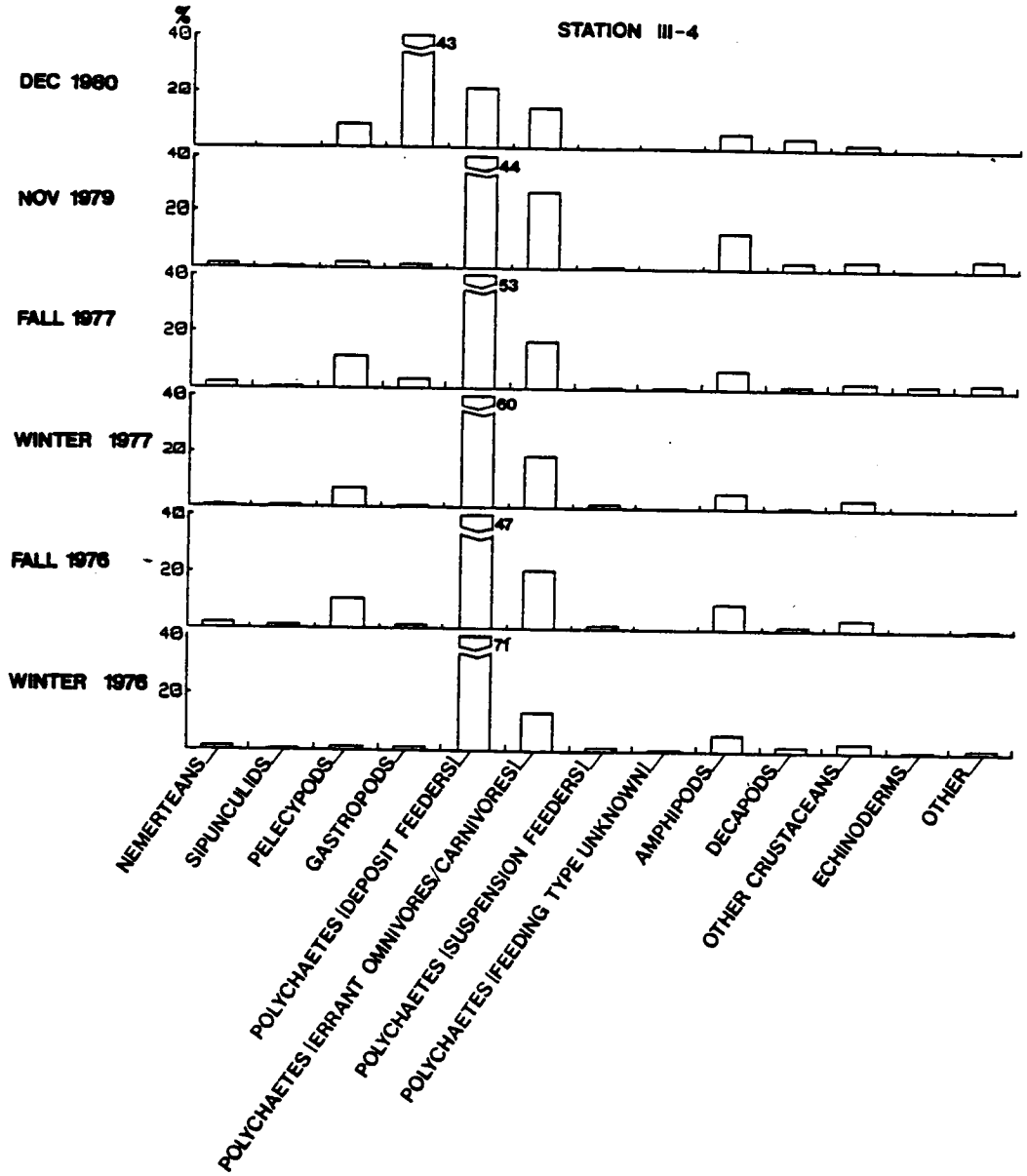


Figure 4-24. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station III-4, by sampling period (1% cutoff).

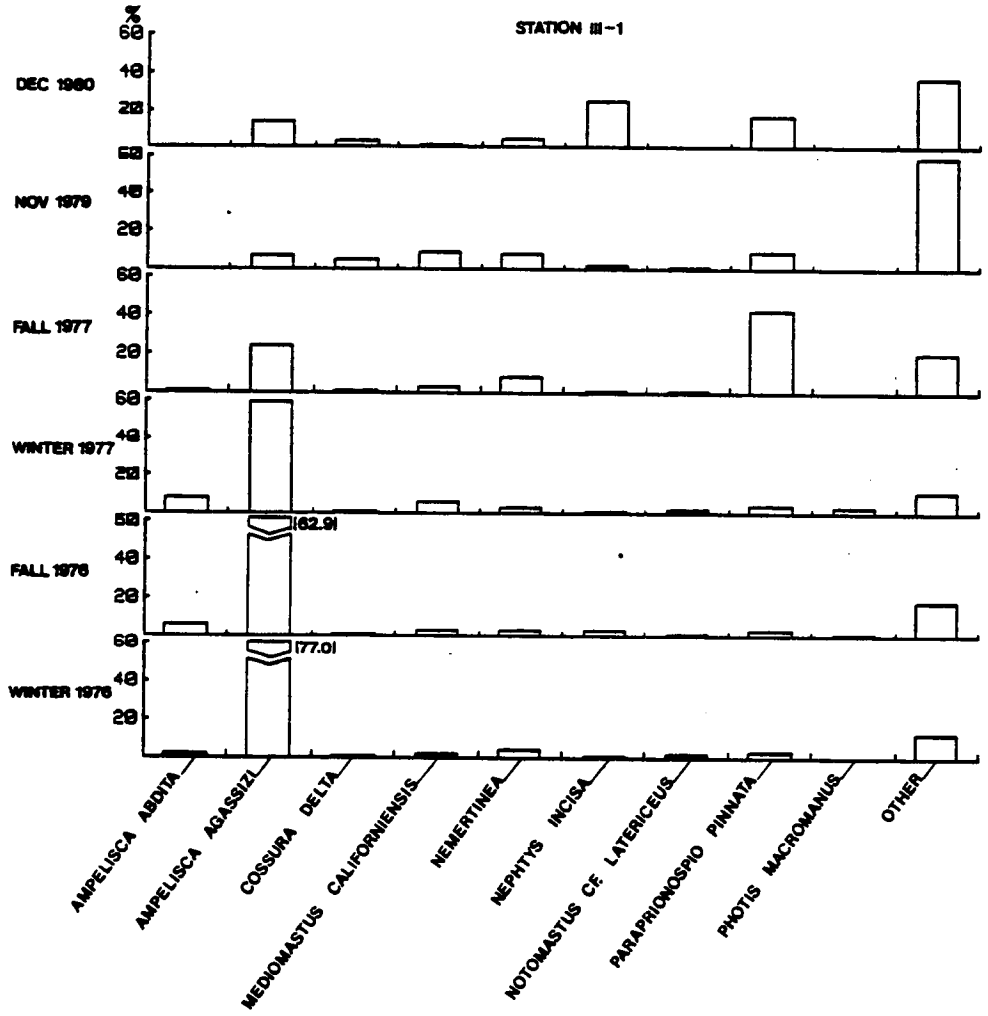


Figure 4-25. Relative proportions of numbers of individuals of numerically dominant taxa at Station III-1, by sampling period (1% cutoff).

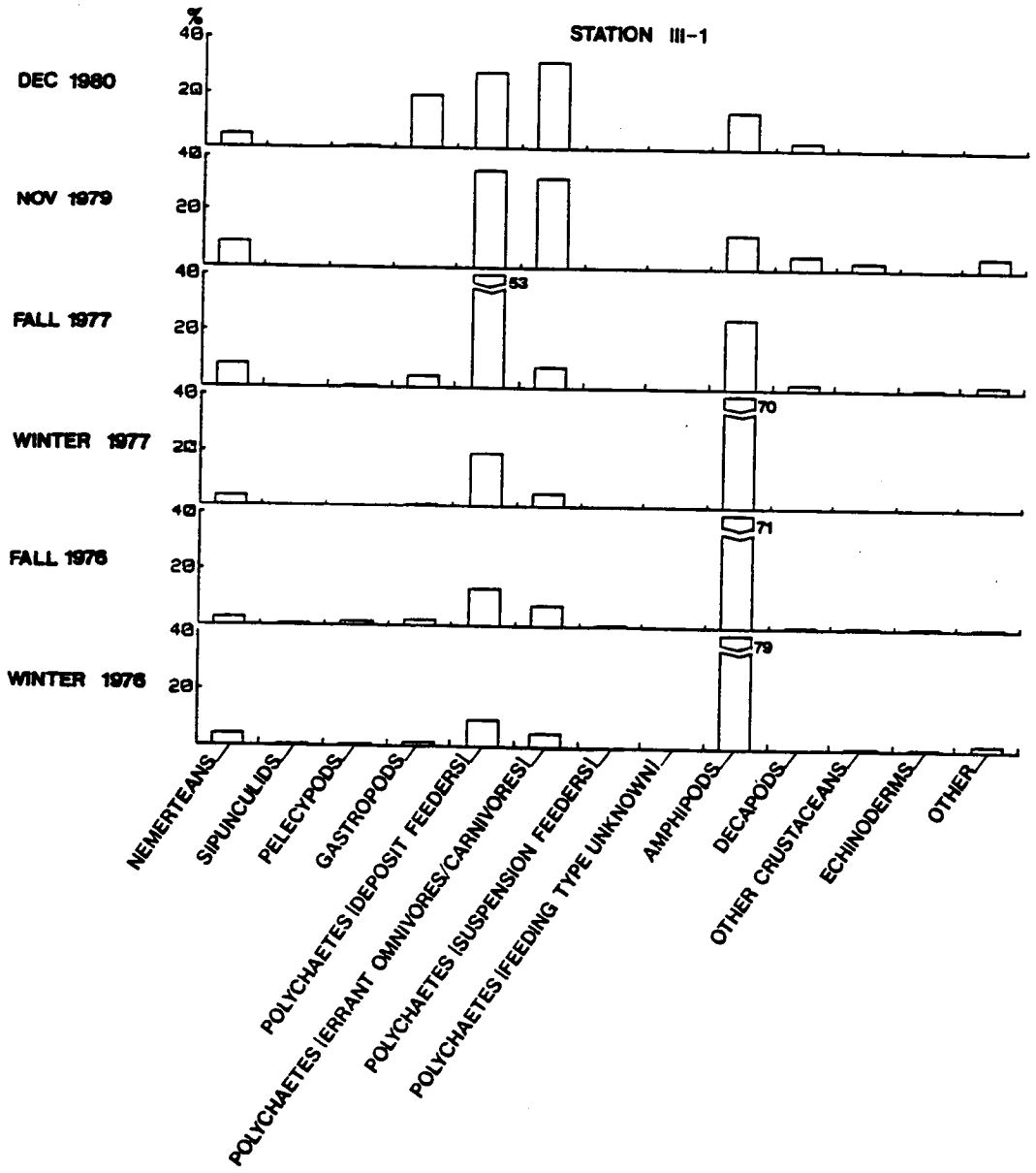


Figure 4-26. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station III-1, by sampling period (1% cutoff).

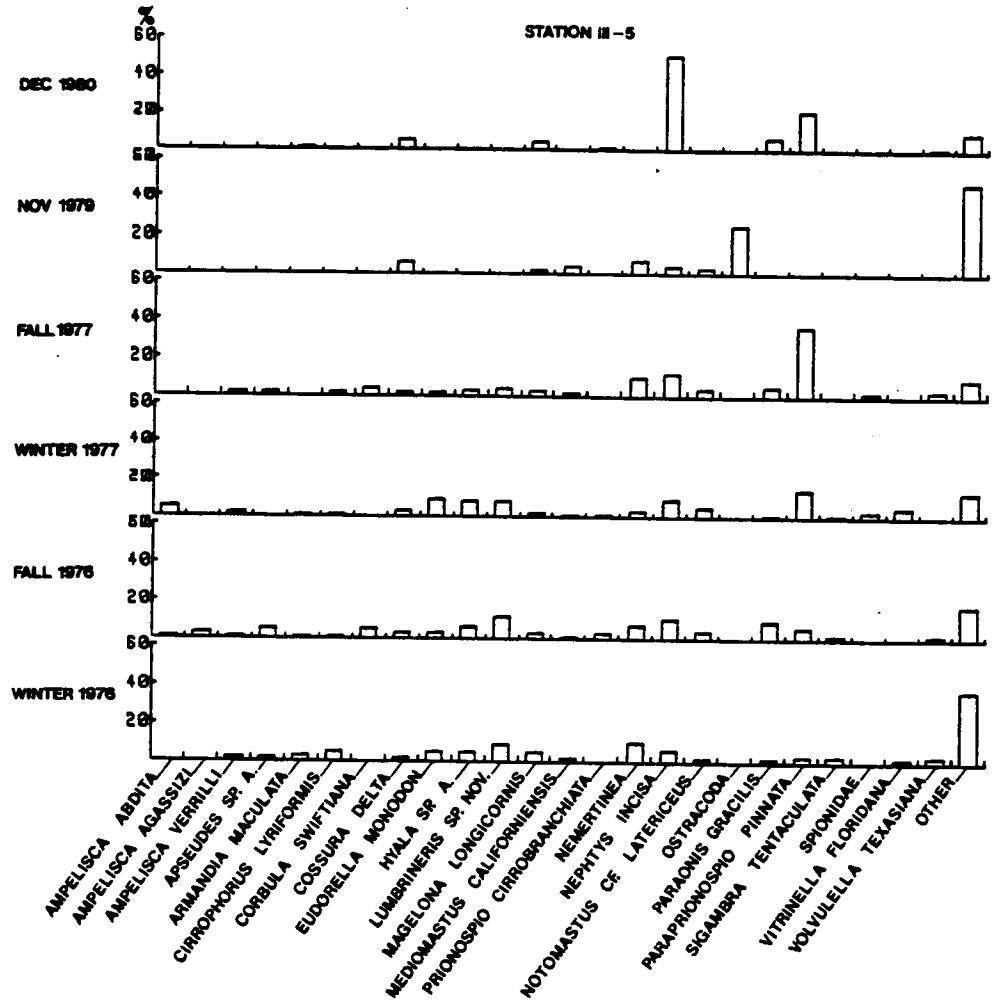


Figure 4-27. Relative proportions of numbers of individuals of numerically dominant taxa at Station III-5, by sampling period (1% cutoff).

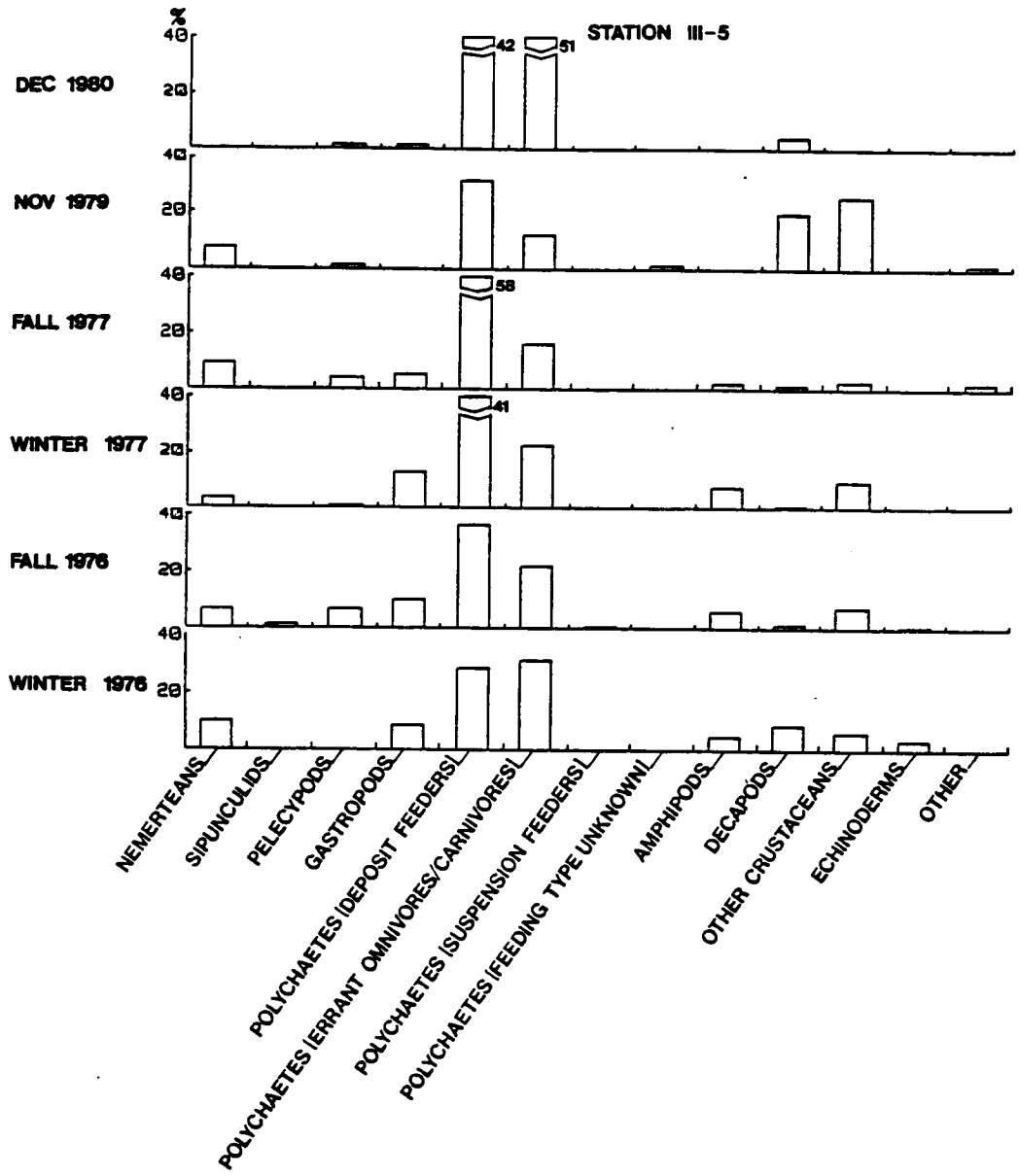


Figure 4-28. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station III-5, by sampling period (1% cutoff).

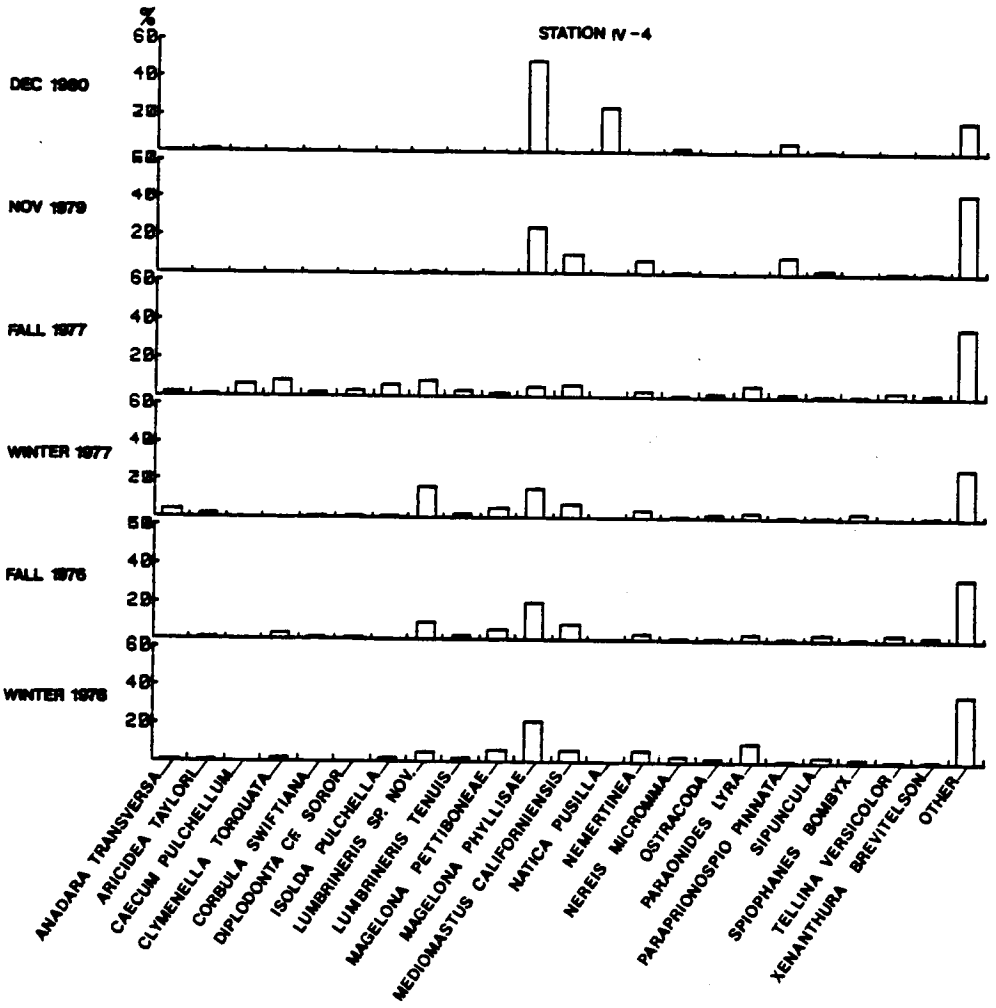


Figure 4-29. Relative proportions of numbers of individuals of numerically dominant taxa at Station IV-4, by sampling period (1% cutoff).

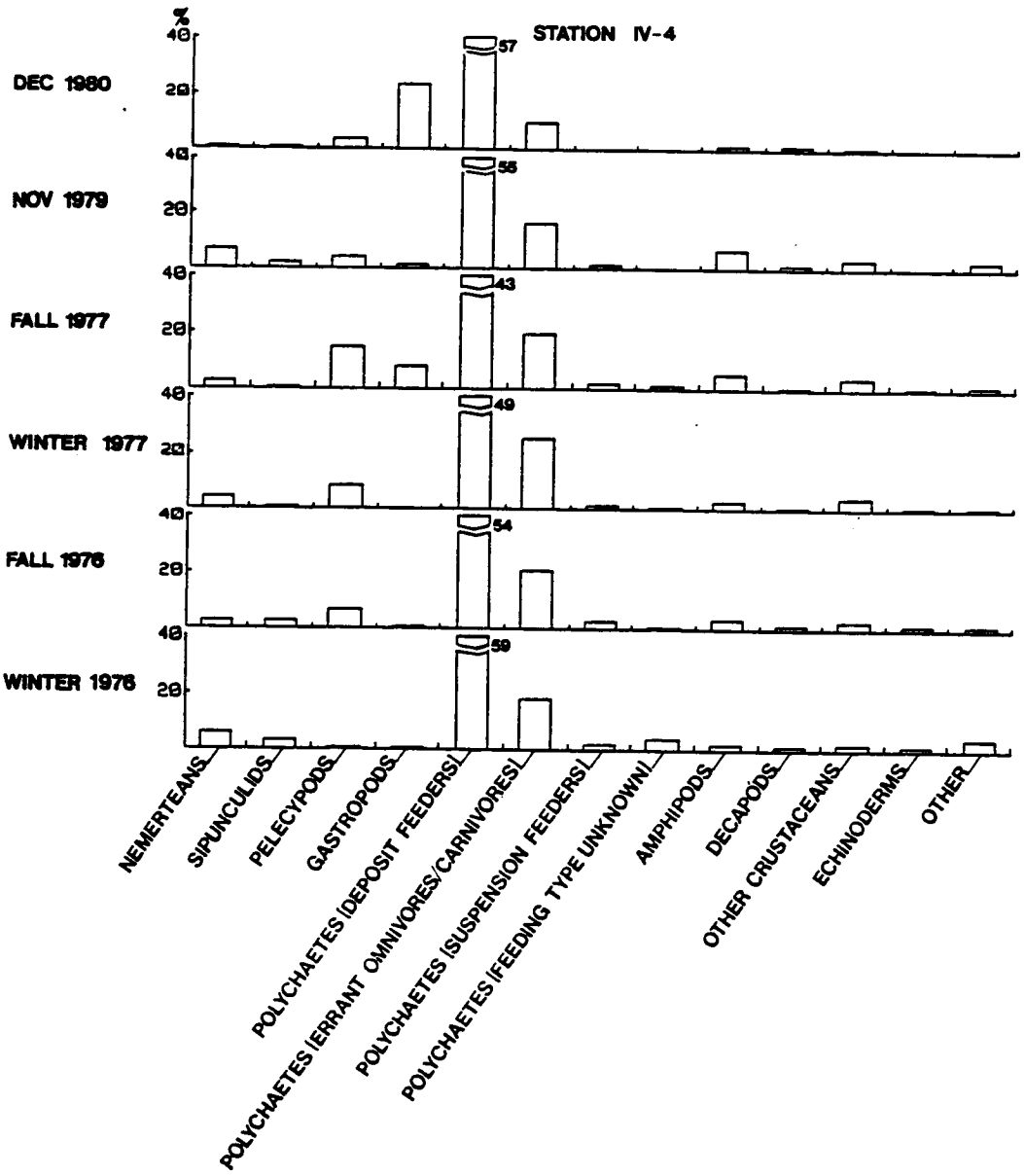


Figure 4-30. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station IV-4, by sampling period (1% cutoff).

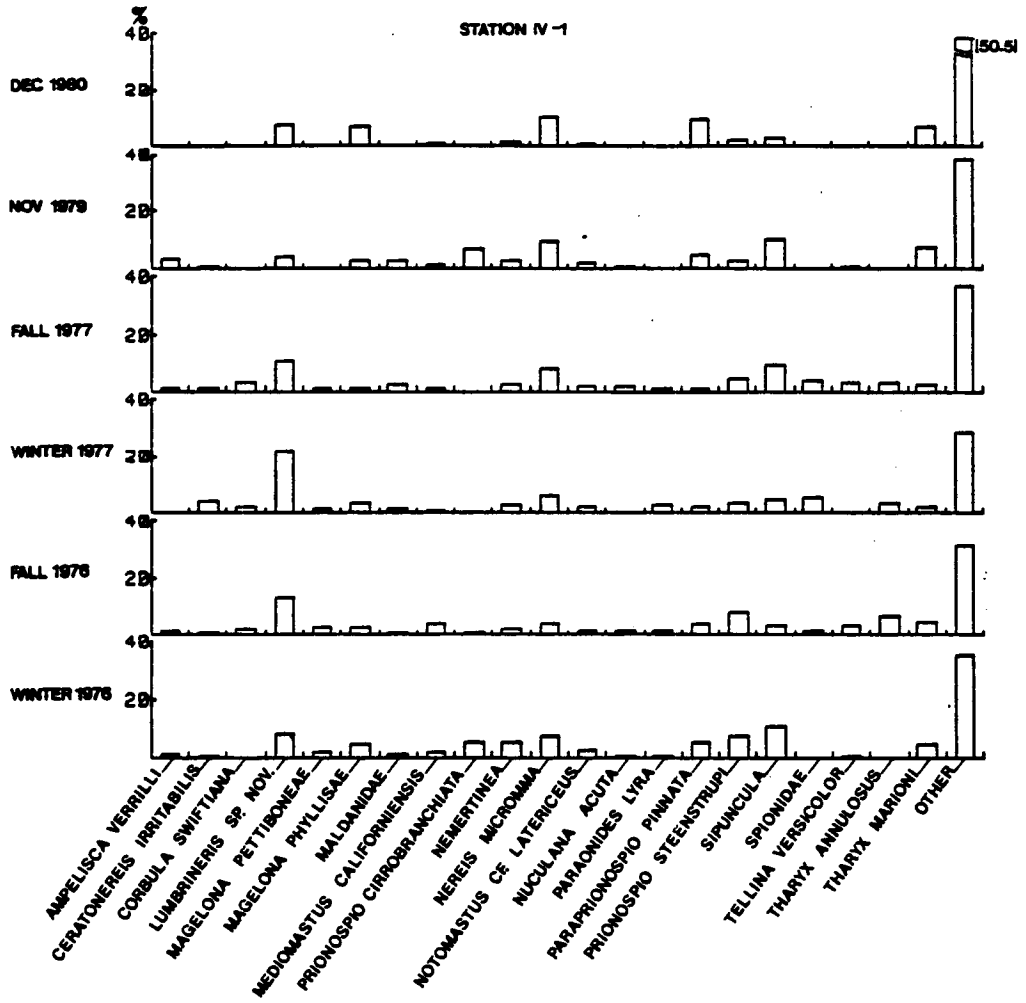


Figure 4-31. Relative proportions of numbers of individuals of numerically dominant taxa at Station IV-1, by sampling period (1% cutoff).

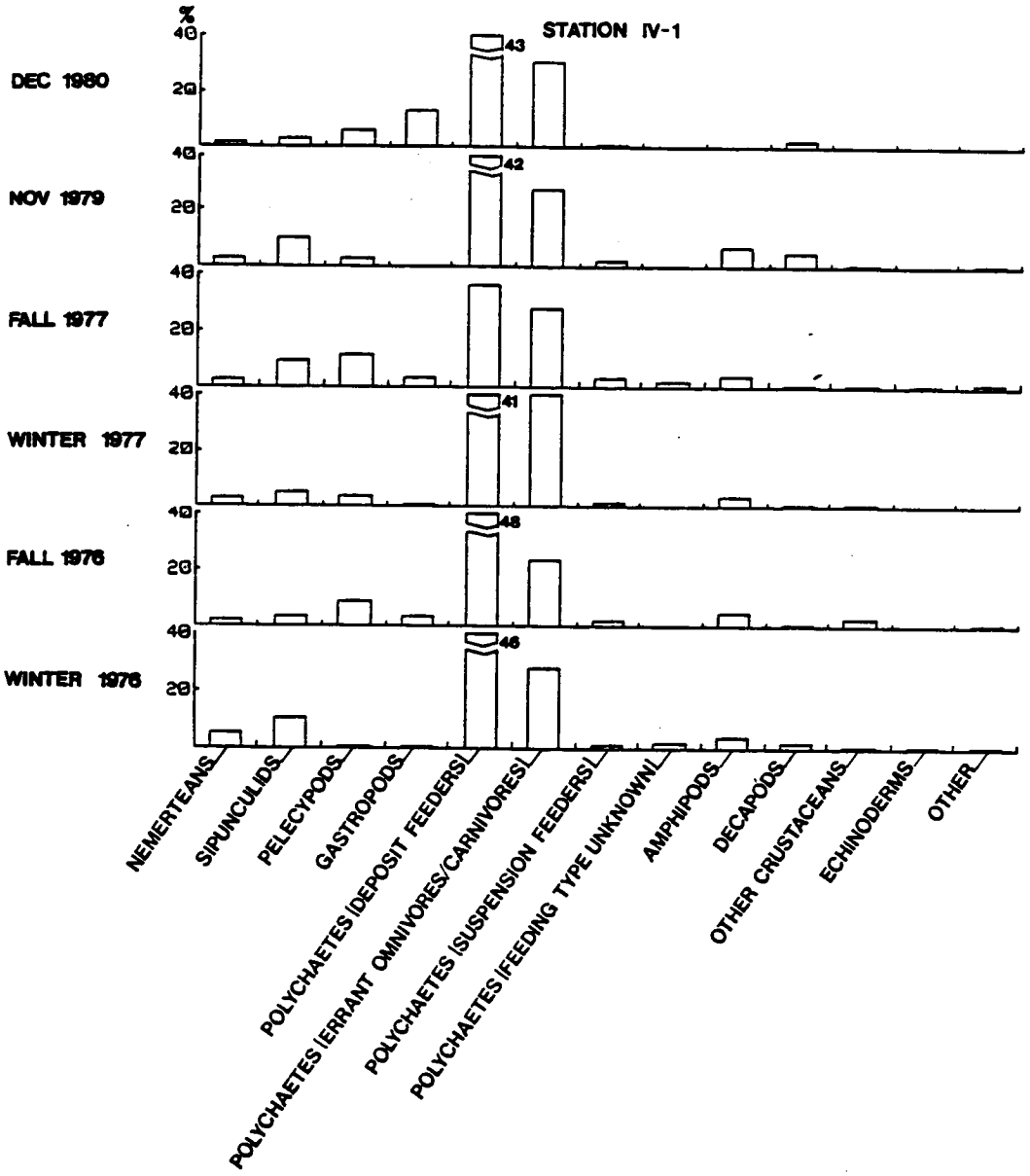


Figure 4-32. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station IV-1, by sampling period (1% cutoff).

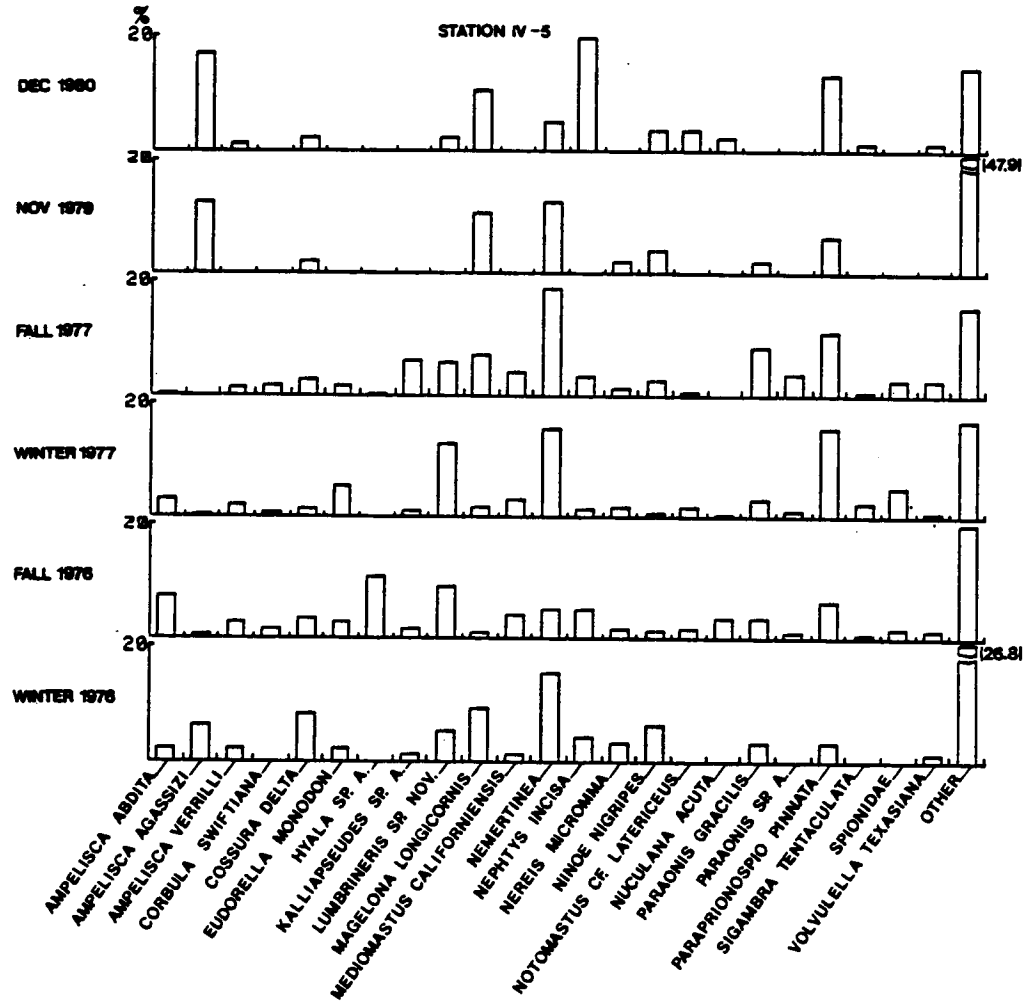


Figure 4-33. Relative proportions of numbers of individuals of numerically dominant taxa at Station IV-5, by sampling period (1% cutoff).

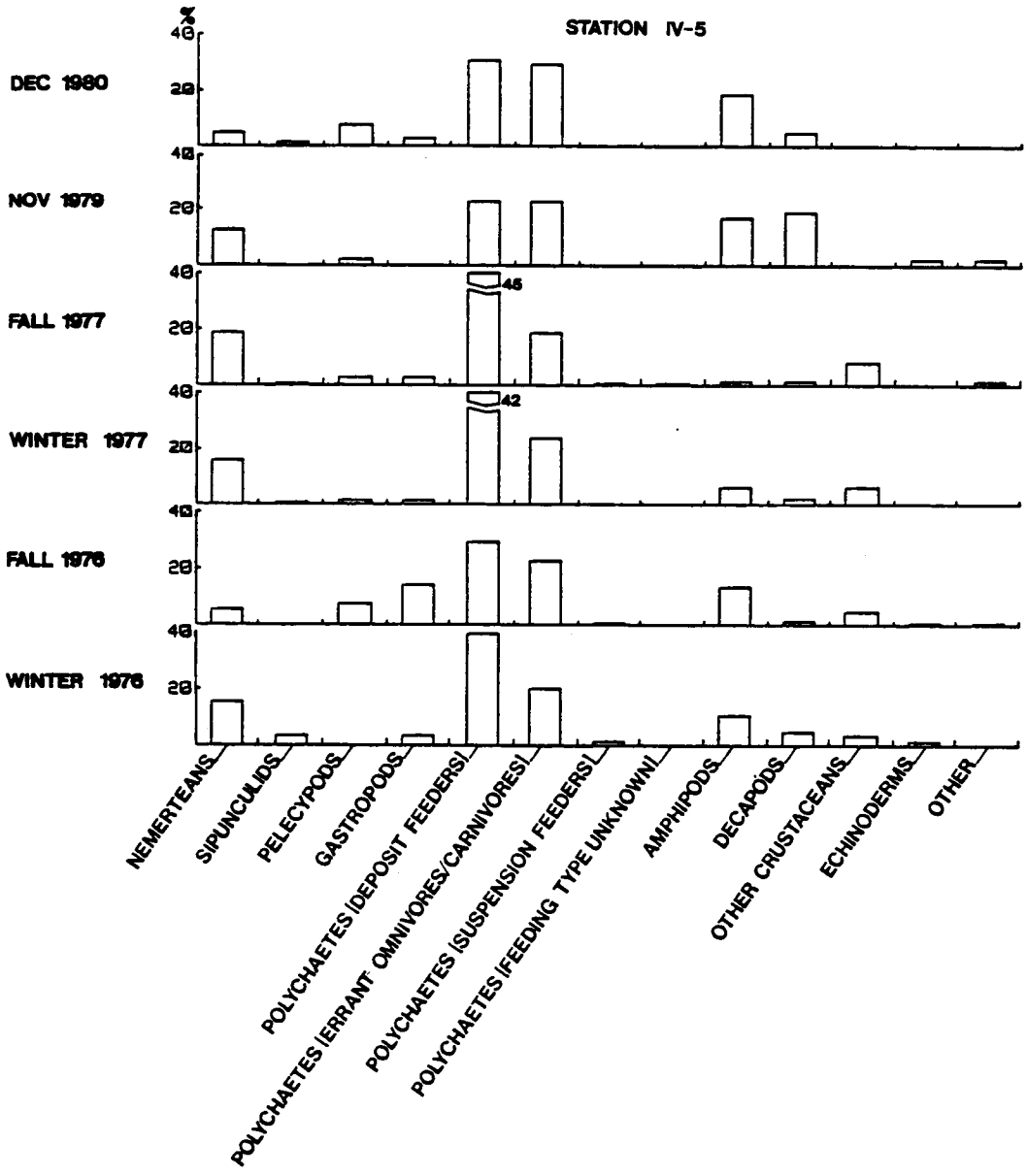


Figure 4-34. Relative proportions of numbers of individuals of major groups of numerically dominant taxa at Station IV-5, by sampling period (1% cutoff).

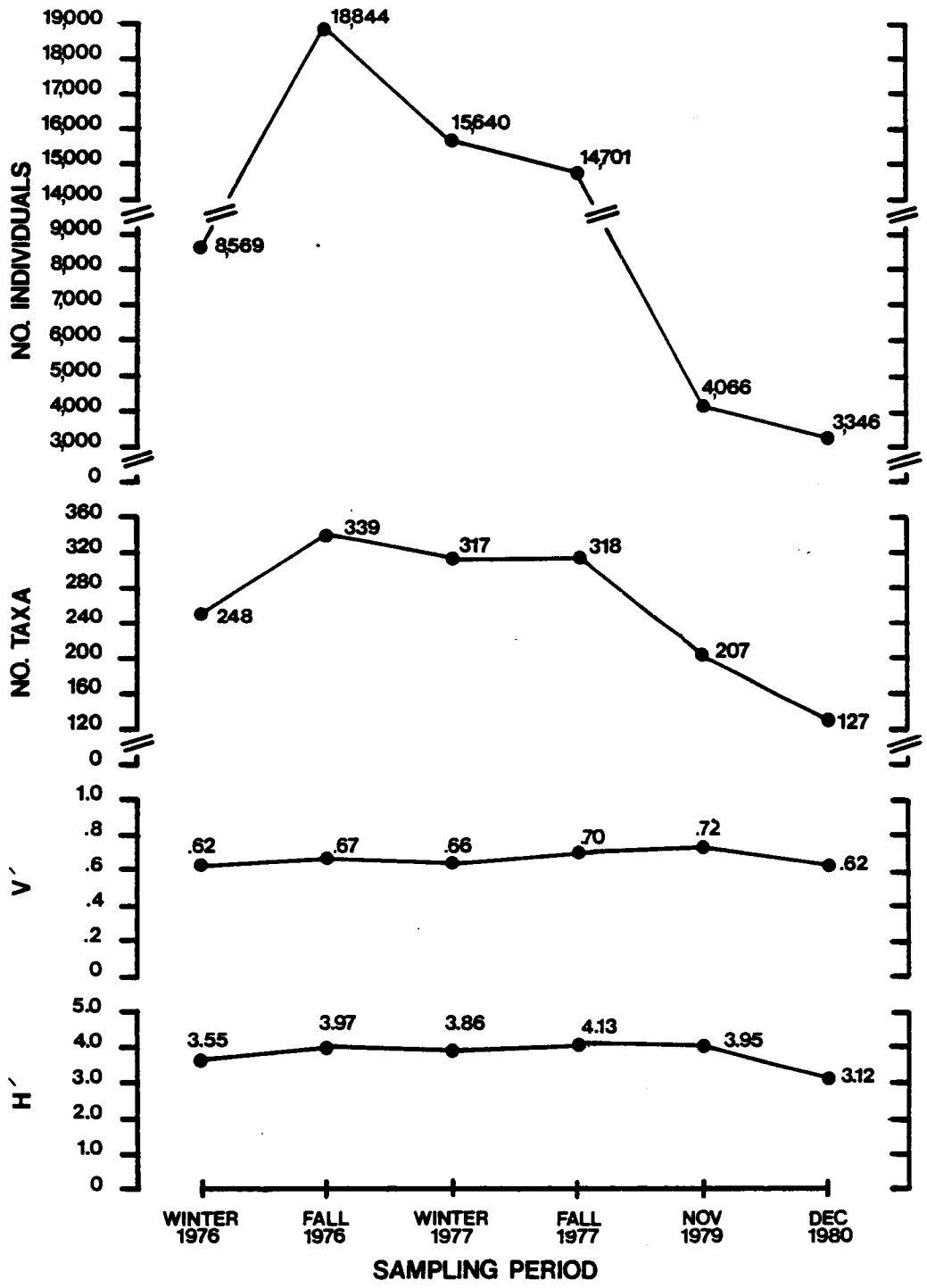


Figure 4-35. Community summary statistics (V', H', number of taxa, number of individuals) for all stations together, by sampling period.

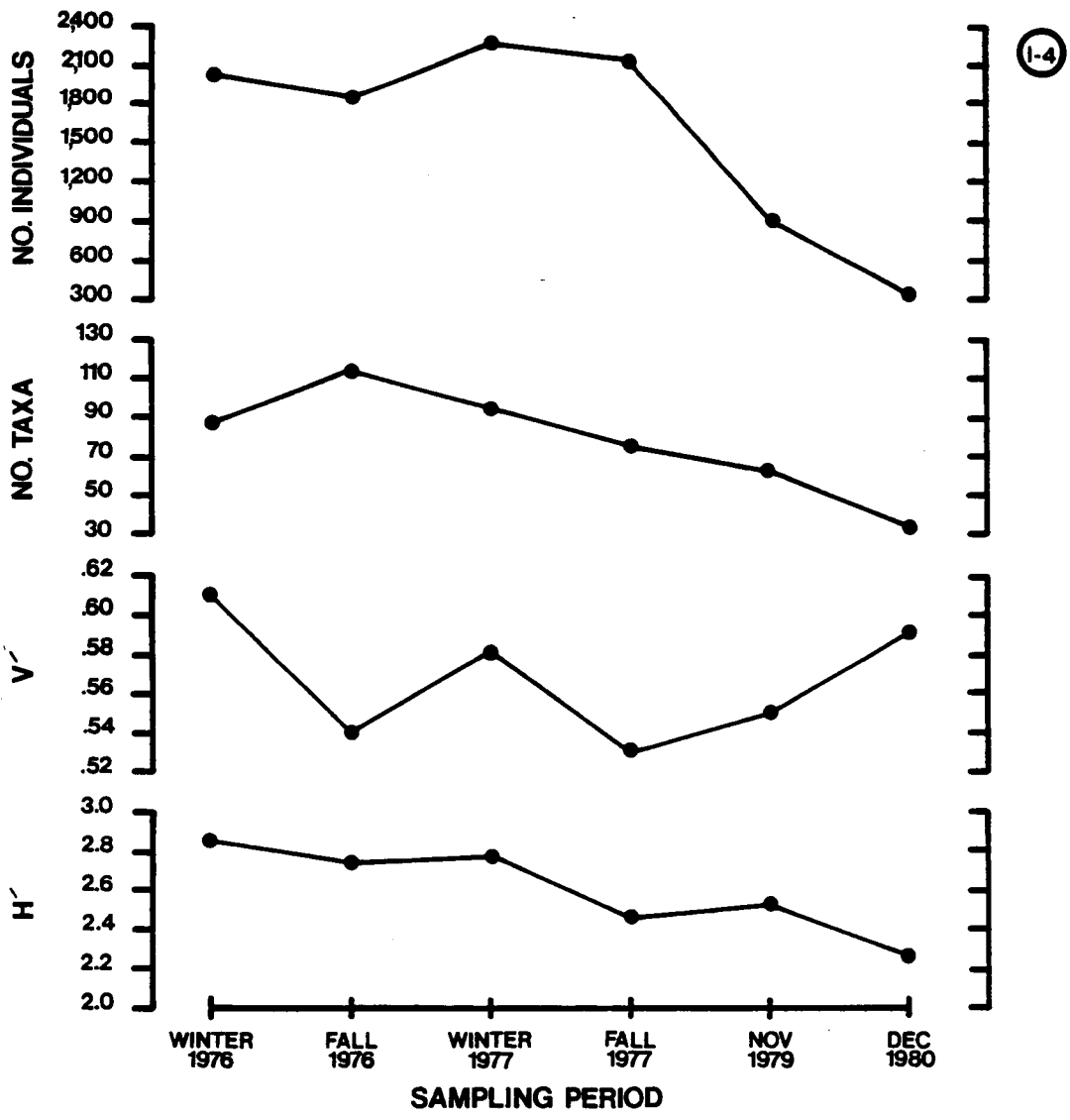


Figure 4-36. Community summary statistics at Station I-4, by sampling period.

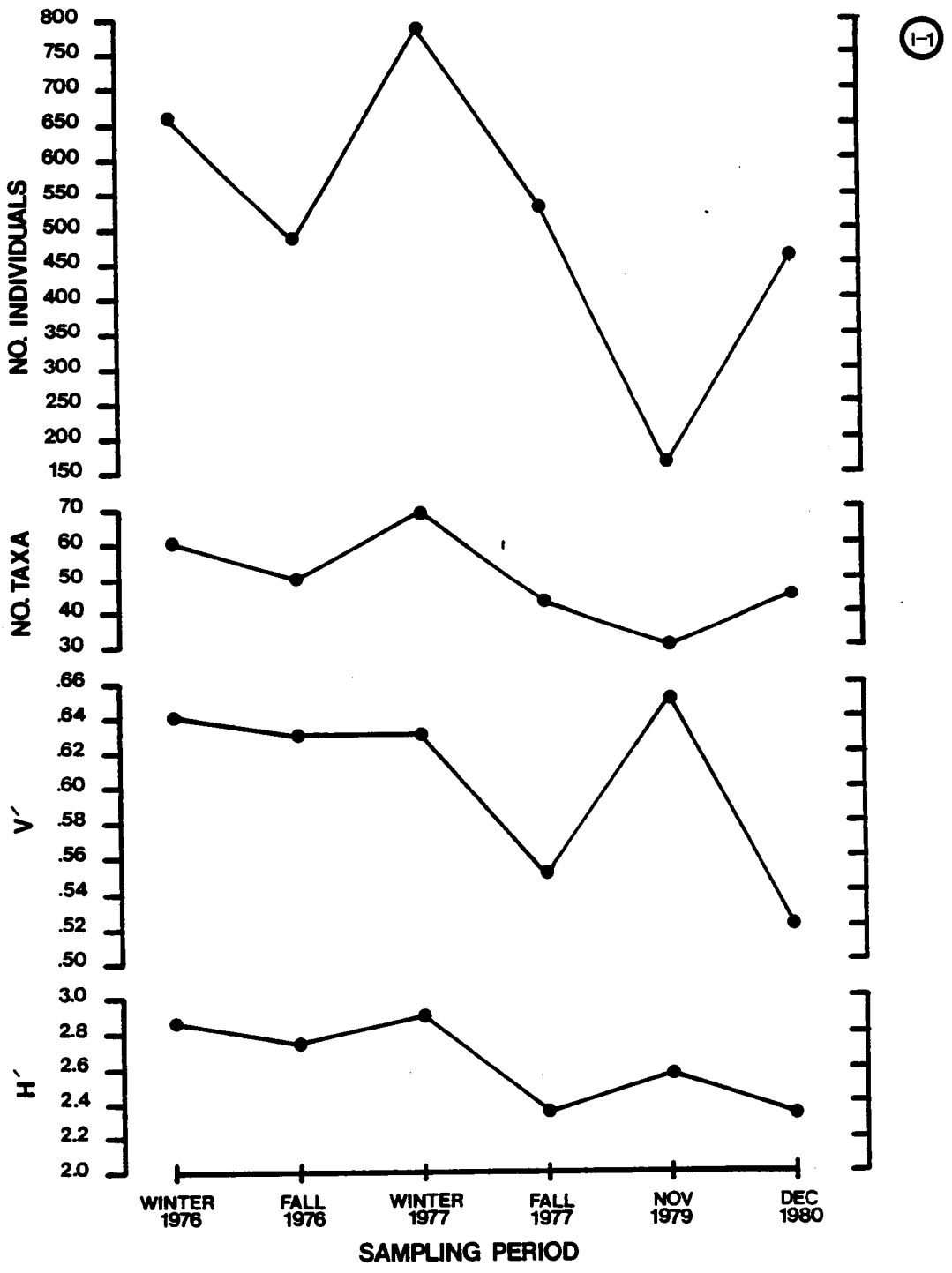


Figure 4-37. Community summary statistics at Station I-1, by sampling period.

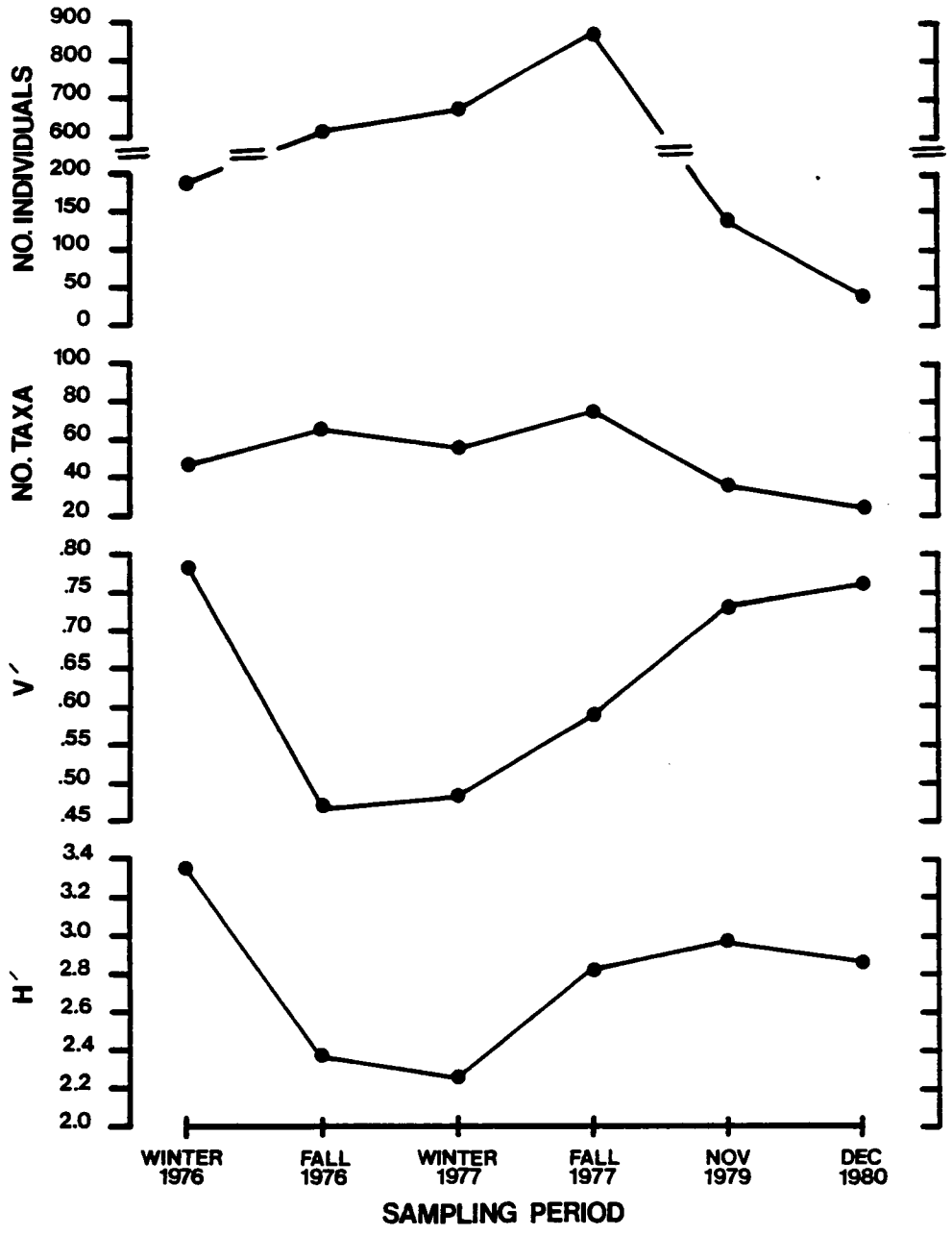


Figure 4-38. Community summary statistics at Station I-2, by sampling period.

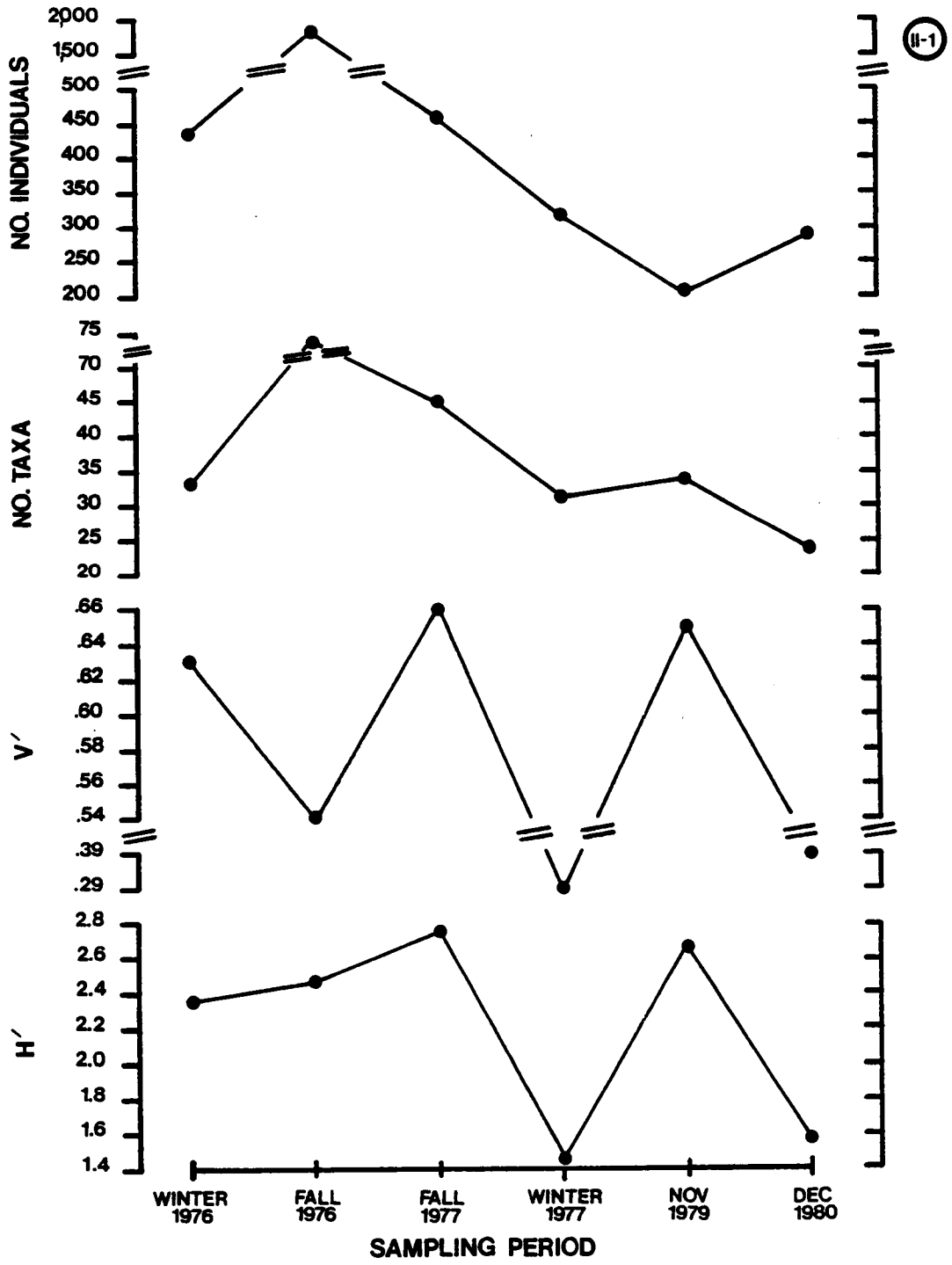


Figure 4-39. Community summary statistics at Station II-1, by sampling period.

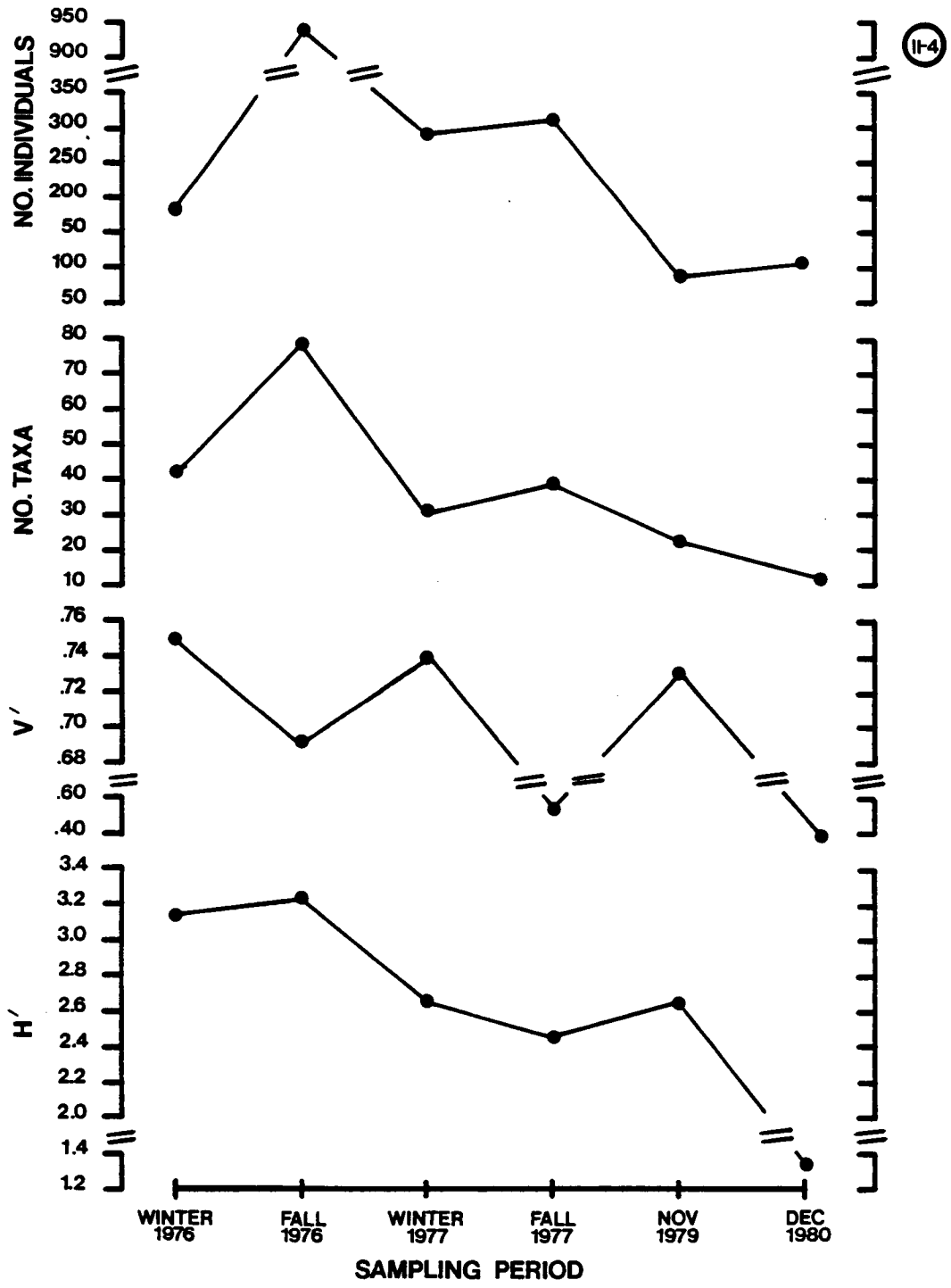


Figure 4-40. Community summary statistics at Station II-4, by sampling period.

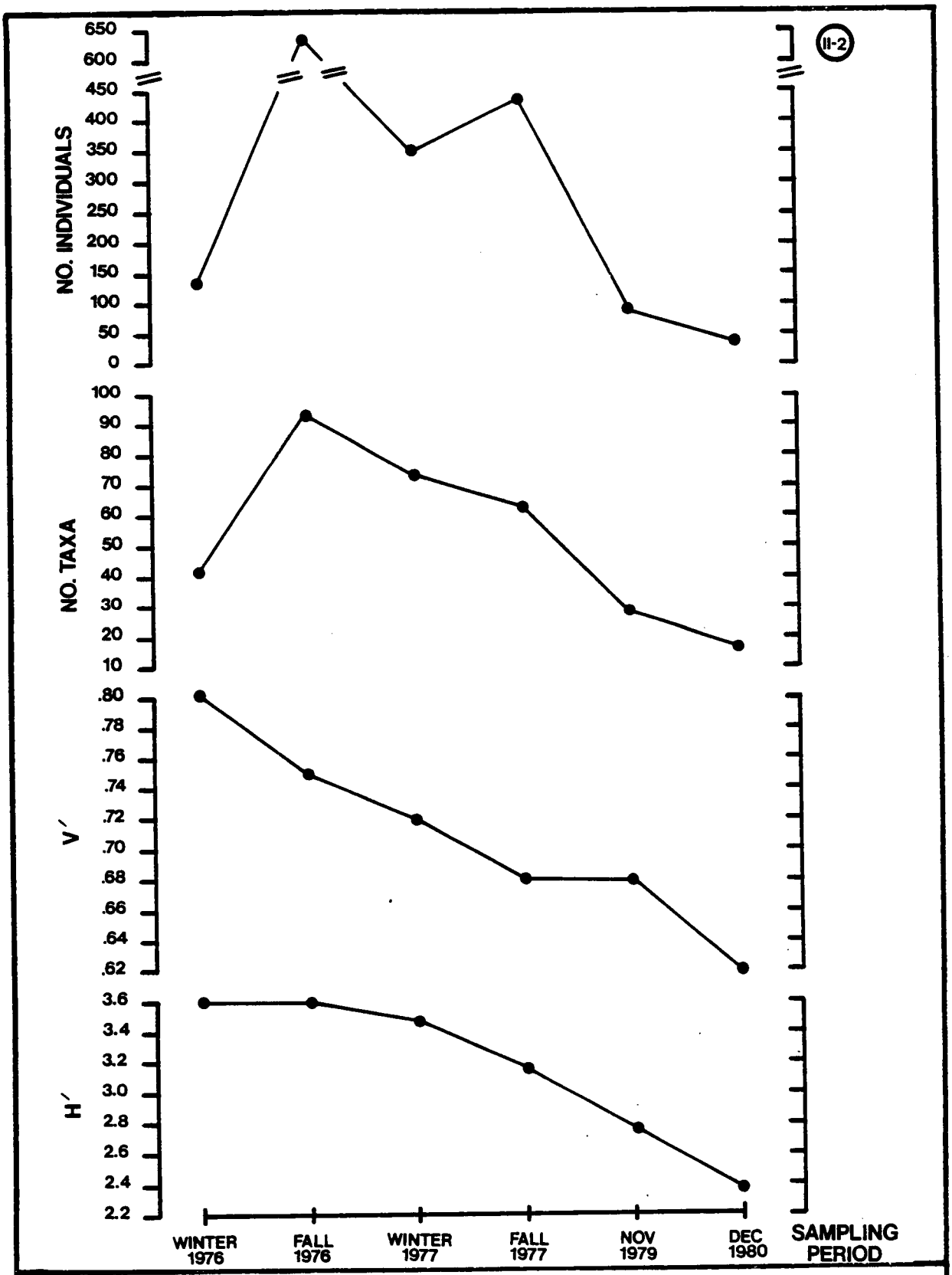


Figure 4-41. Community summary statistics at Station II-2, by sampling period.

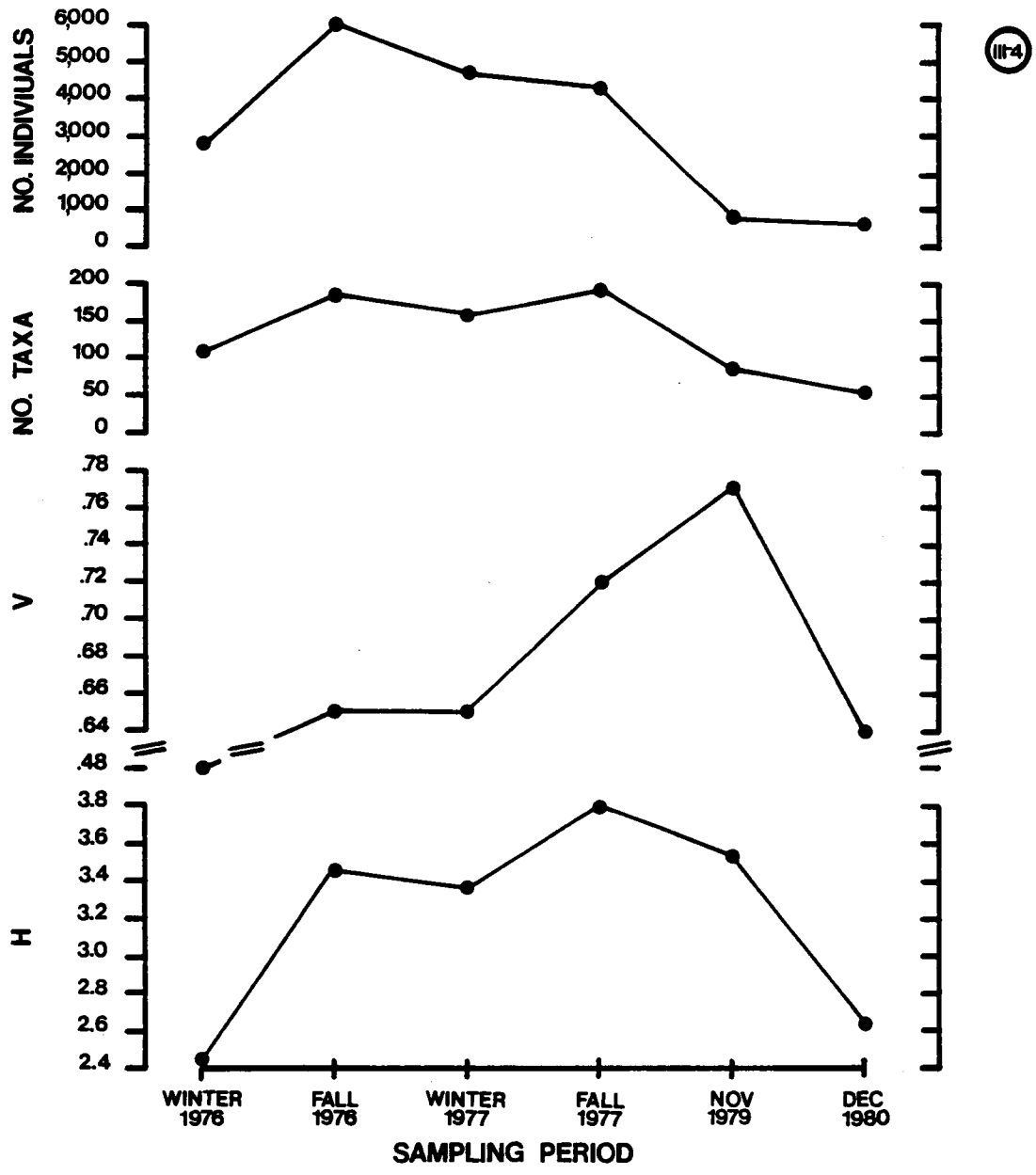


Figure 4-42. Community summary statistics at Station III-4, by sampling period.

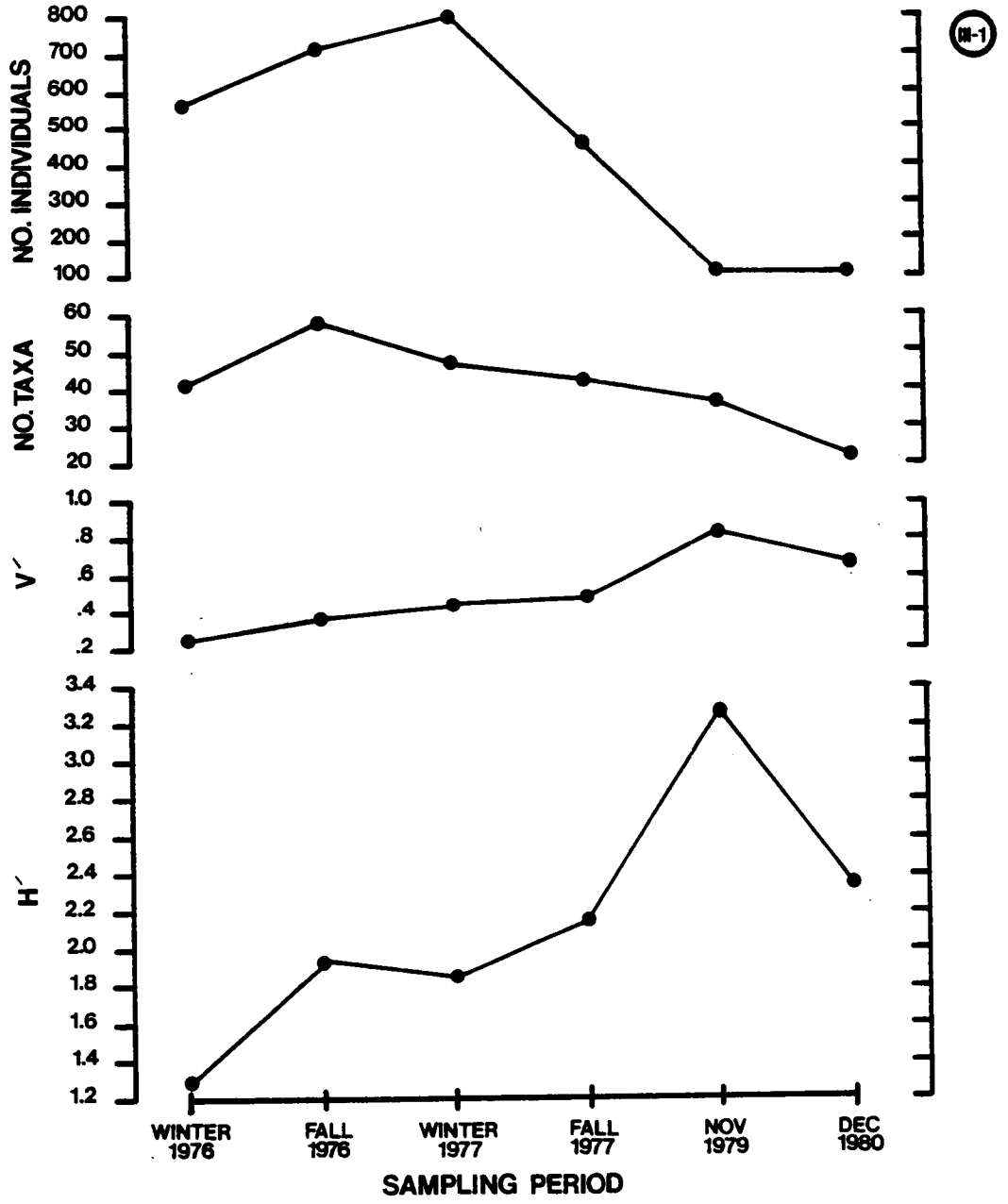


Figure 4-43. Community summary statistics at Station III-1, by sampling period.

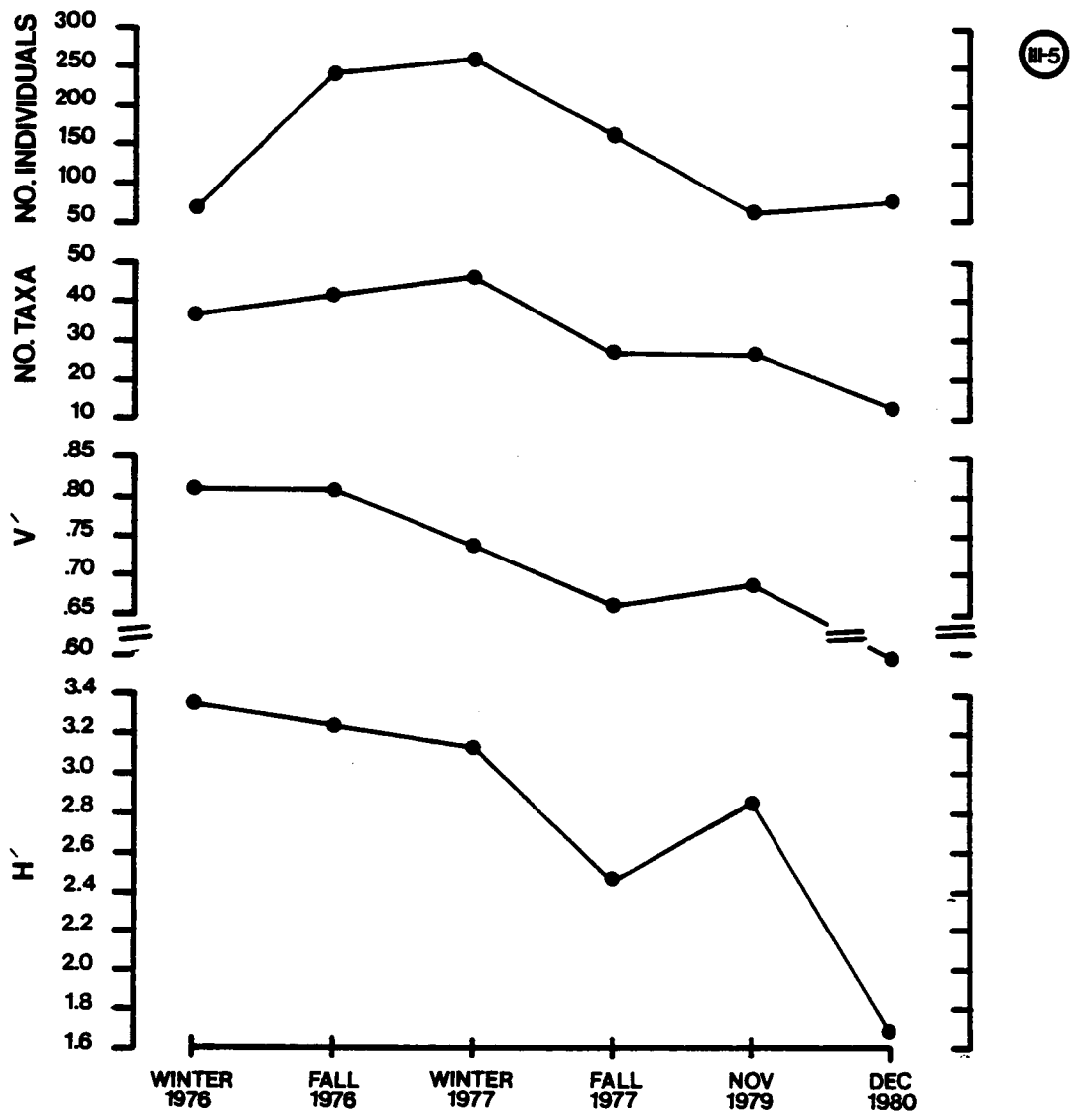


Figure 4-44. Community summary statistics at Station III-5, by sampling period.

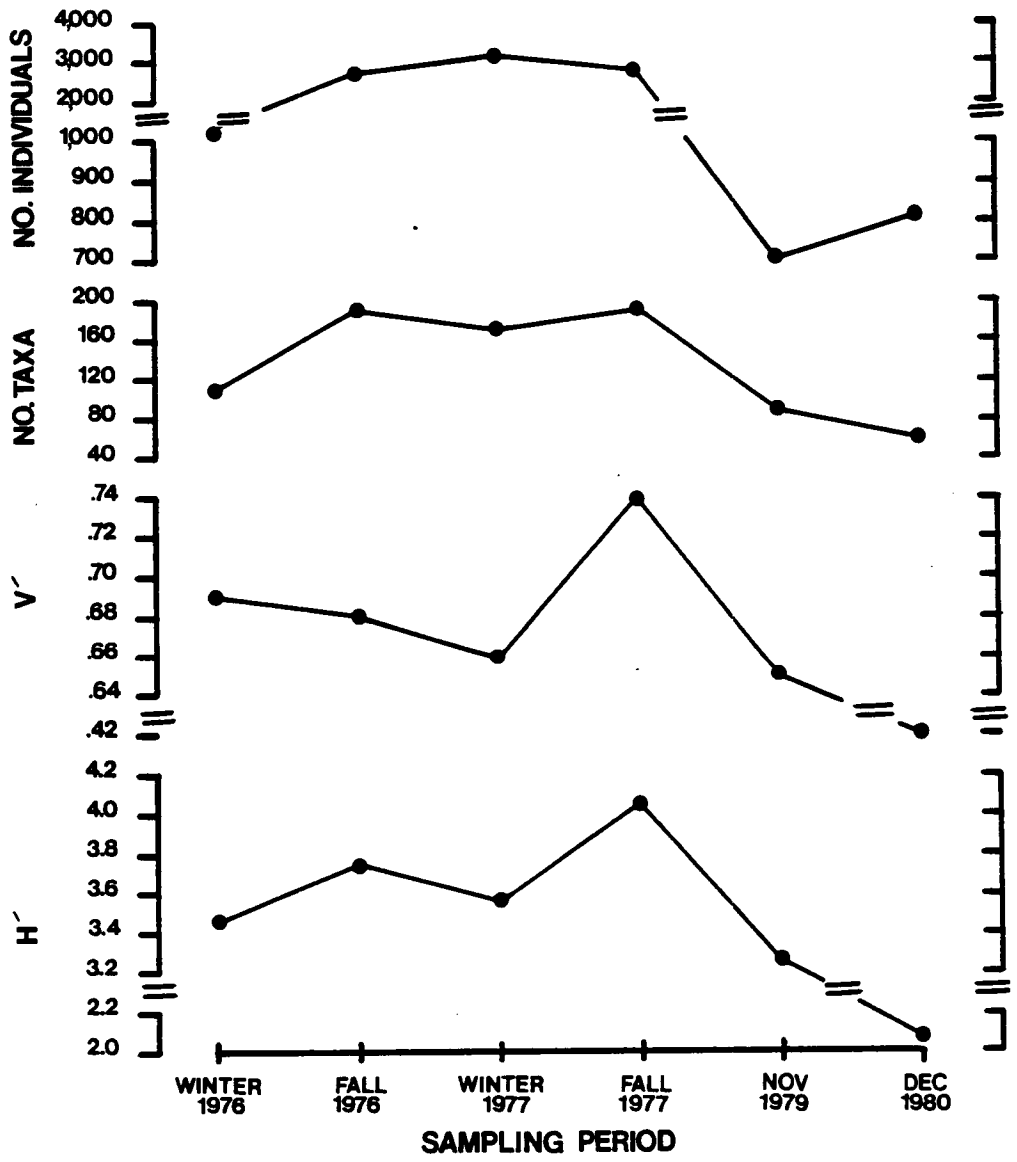


Figure 4-45. Community summary statistics at Station IV-4, by sampling period.

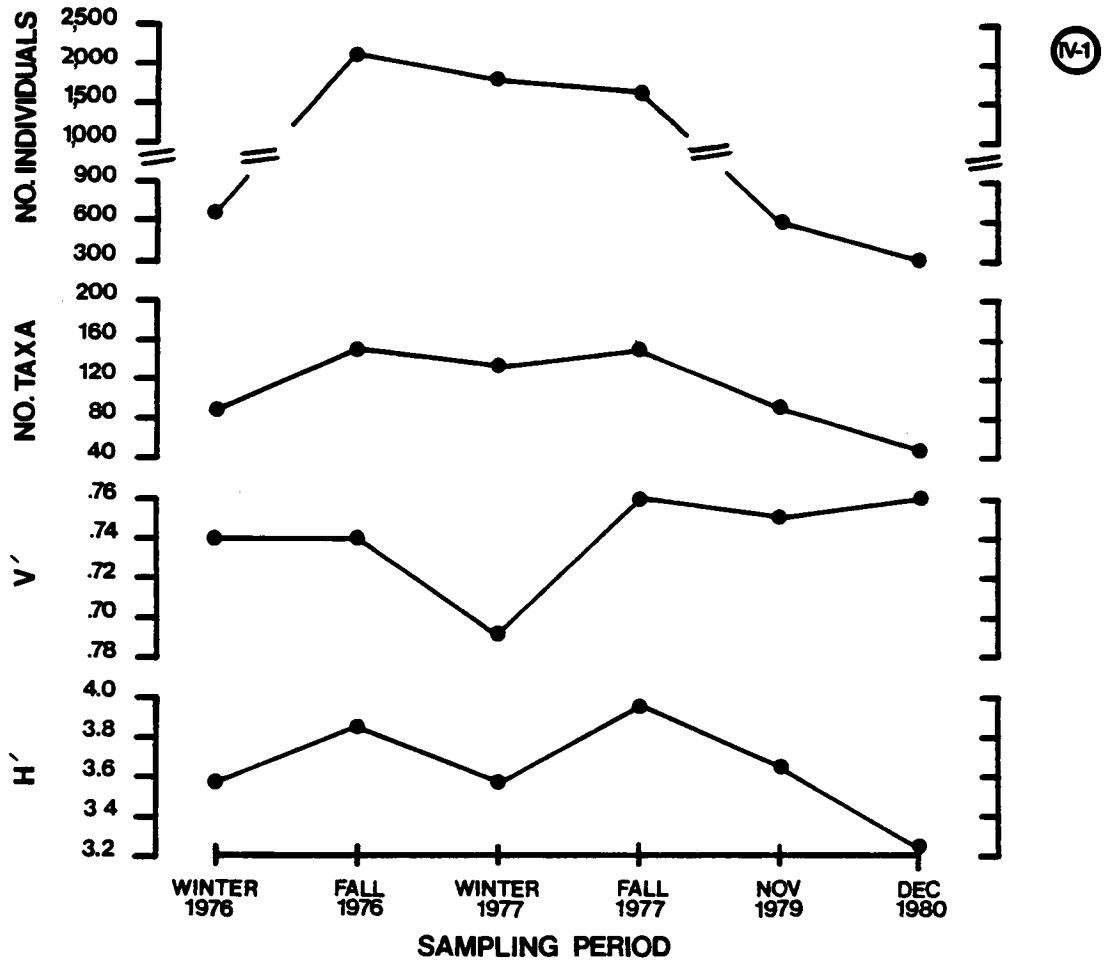


Figure 4-46. Community summary statistics at Station IV-1, by sampling period.

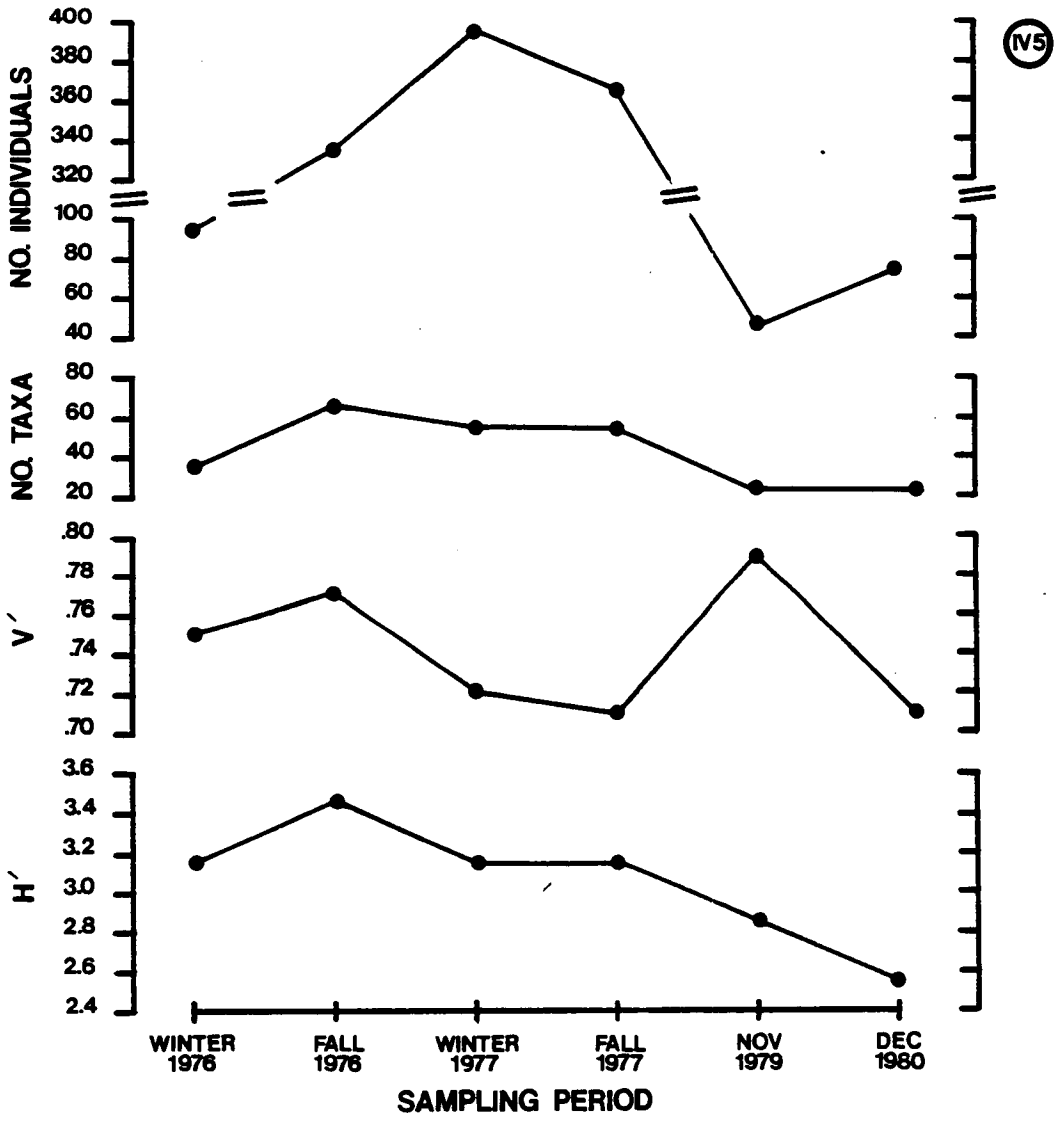


Figure 4-47. Community summary statistics at Station IV-5, by sampling period.

Table 4-4. Number of individuals, number of taxa, evenness (V') and diversity (H') at each station, by sampling period.

Number of Individuals

Station	Winter 76	Fall 77	Winter 77	Fall 77	Nov 79	Dec 80
I-4	2037	1865	2283	2143	900	396
I-1	668	491	789	526	164	458
I-2	197	606	668	860	135	47
II-1	442	1861	454	323	206	282
II-4	176	940	297	318	88	101
II-2	139	645	350	434	89	38
III-4	2095	6023	4635	4475	944	660
III-1	557	707	821	454	106	103
III-5	70	247	266	158	67	74
IV-4	1439	2875	3084	2947	702	818
IV-1	652	2249	1596	1695	617	293
IV-5	97	335	397	368	48	76

Number of Taxa

I-4	88	112	94	75	62	33
I-1	60	50	69	43	30	45
I-2	49	66	57	75	35	23
II-1	33	74	45	32	34	24
II-4	41	79	30	39	23	12
II-2	43	94	74	64	28	16
III-4	102	179	159	195	82	54
III-1	41	58	47	43	37	21
III-5	36	42	46	26	27	13
IV-4	110	191	174	194	92	61
IV-1	89	151	131	146	91	49
IV-5	36	64	54	55	21	21

Evenness (V')

I-4	.61	.54	.58	.53	.55	.59
I-1	.64	.63	.63	.55	.65	.52
I-2	.78	.47	.48	.59	.73	.76
II-1	.63	.54	.67	.29	.65	.40
II-4	.75	.69	.74	.57	.73	.39
II-2	.81	.75	.72	.68	.68	.62
III-4	.48	.65	.65	.72	.77	.60
III-1	.24	.38	.42	.48	.82	.64
III-5	.81	.81	.74	.66	.70	.49
IV-4	.69	.68	.66	.74	.65	.42
IV-1	.74	.74	.69	.76	.75	.76
IV-5	.74	.77	.72	.71	.80	.71

Table 4-4 (cont'd)

Diversity (H')

I-4	2.87	2.77	2.79	2.44	2.52	2.28
I-1	2.86	2.73	2.90	2.32	2.59	2.31
I-2	3.37	2.38	2.26	2.82	3.00	2.89
II-1	2.39	2.49	2.77	1.46	2.64	1.59
II-4	3.13	3.22	2.67	2.44	2.66	1.33
II-2	3.38	3.66	3.49	3.15	2.79	2.38
III-4	2.42	3.49	3.39	3.89	3.53	2.62
III-1	1.29	1.92	1.86	2.15	3.29	2.33
III-5	3.37	3.24	3.12	2.47	2.88	1.68
IV-4	3.43	3.75	3.57	4.03	3.26	2.05
IV-1	3.59	3.84	3.58	3.97	3.65	3.21
IV-5	3.17	3.48	3.13	3.14	2.82	2.56

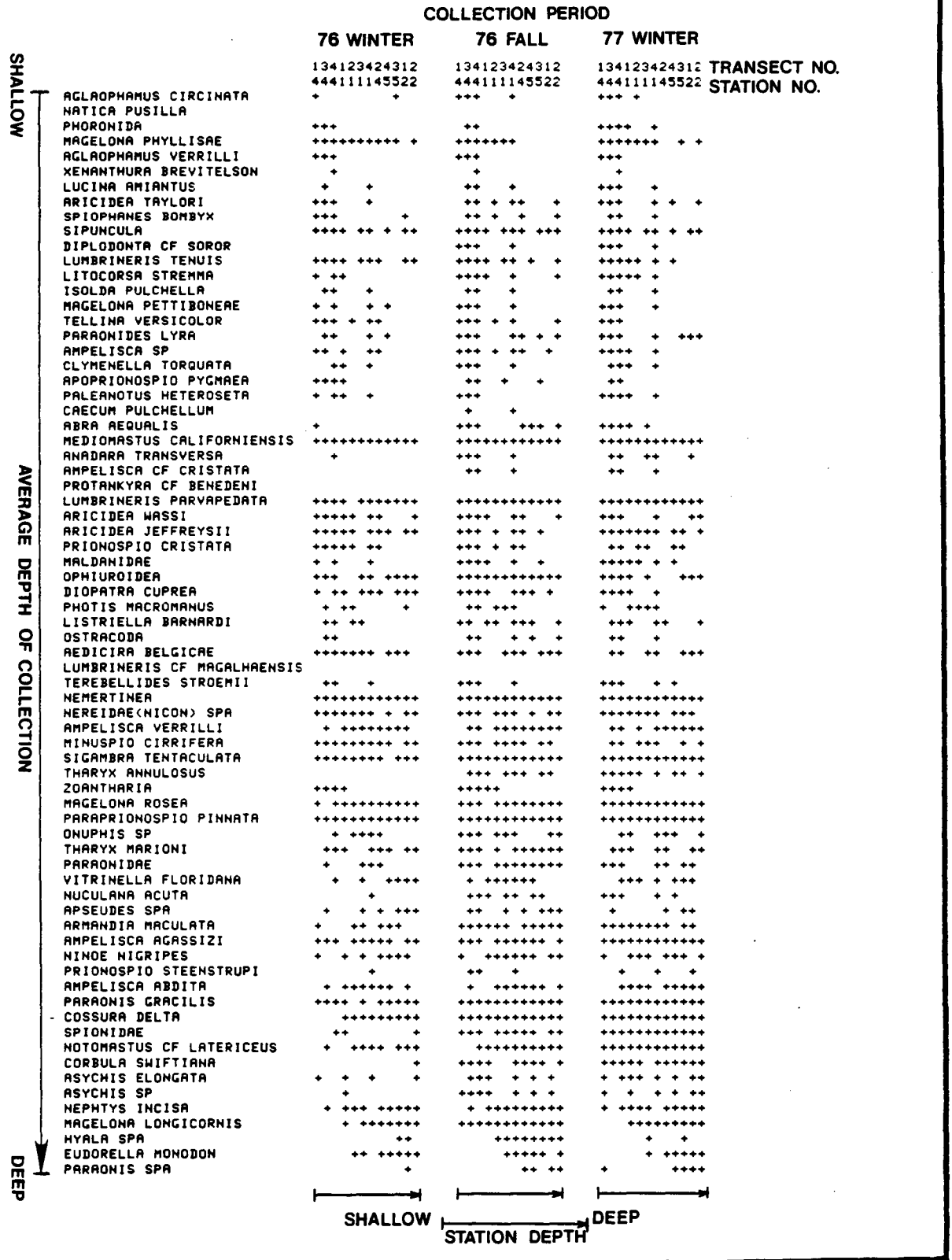


Figure 4-48. Presence (+) of numerically dominant taxa (listed top to bottom in order of increasing collection depth) during six collection periods (in chronological order left to right) at twelve stations (listed left to right by increasing depth, within each collection period) (0.2%) cutoff) (see text for explanation).

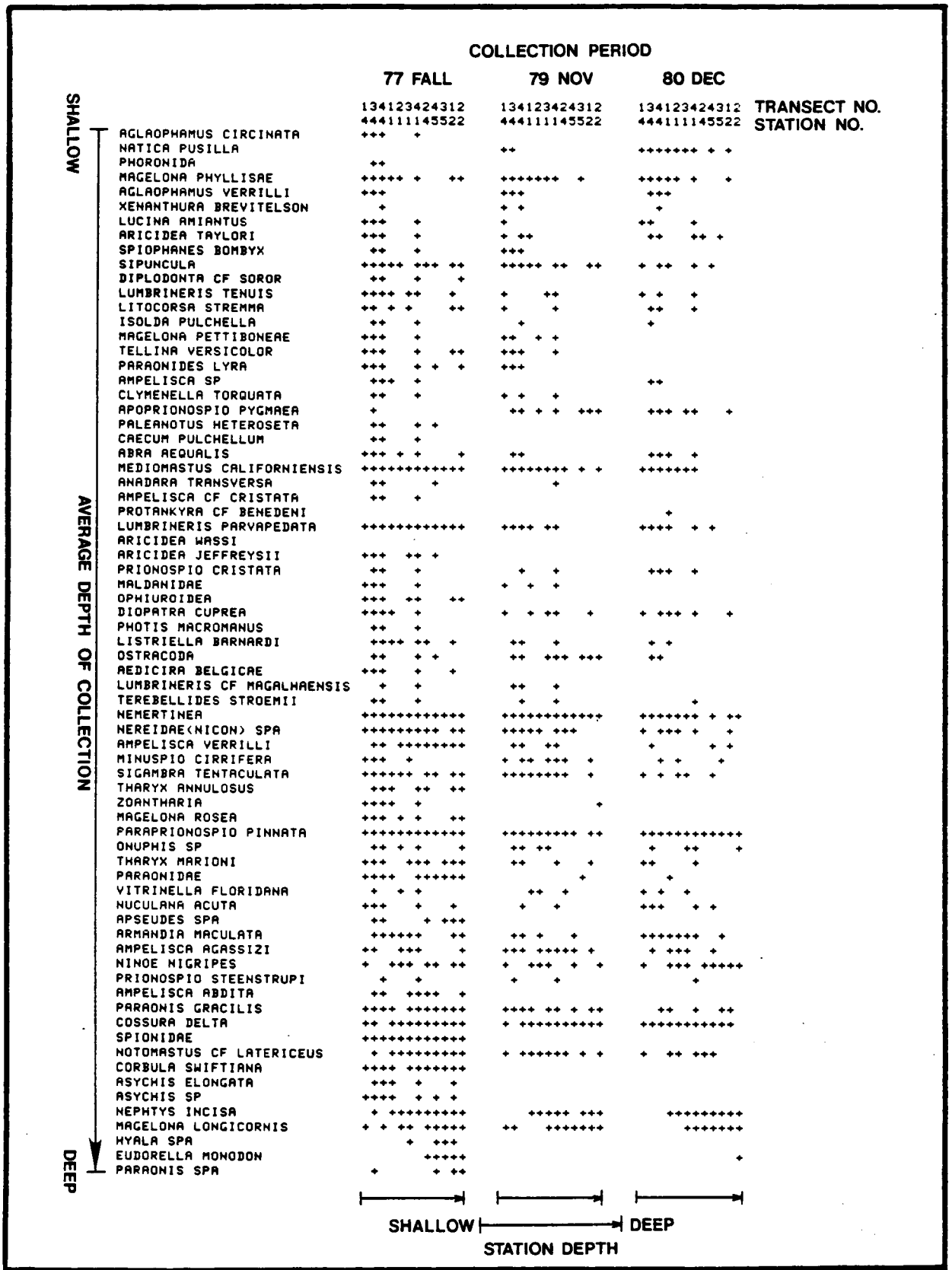


Figure 4-48 (cont'd).

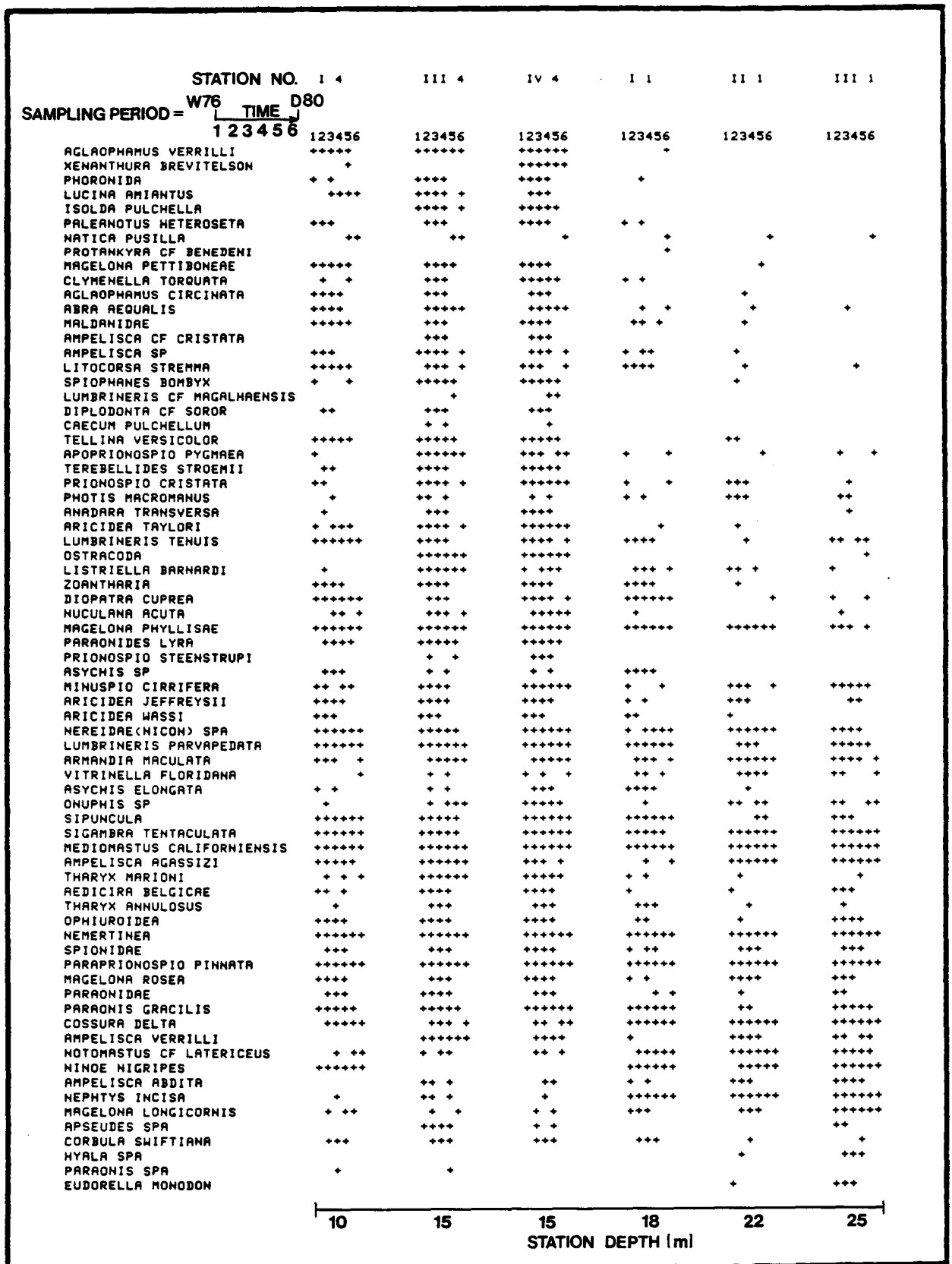


Figure 4-49. Presence (+) of numerically dominant taxa (listed top to bottom in order of increasing collection depth) at each of twelve stations (listed left to right by increasing depth) during six collection periods (listed one-siz in chronological order for each station) (0.2% cutoff) (see text for explanation).

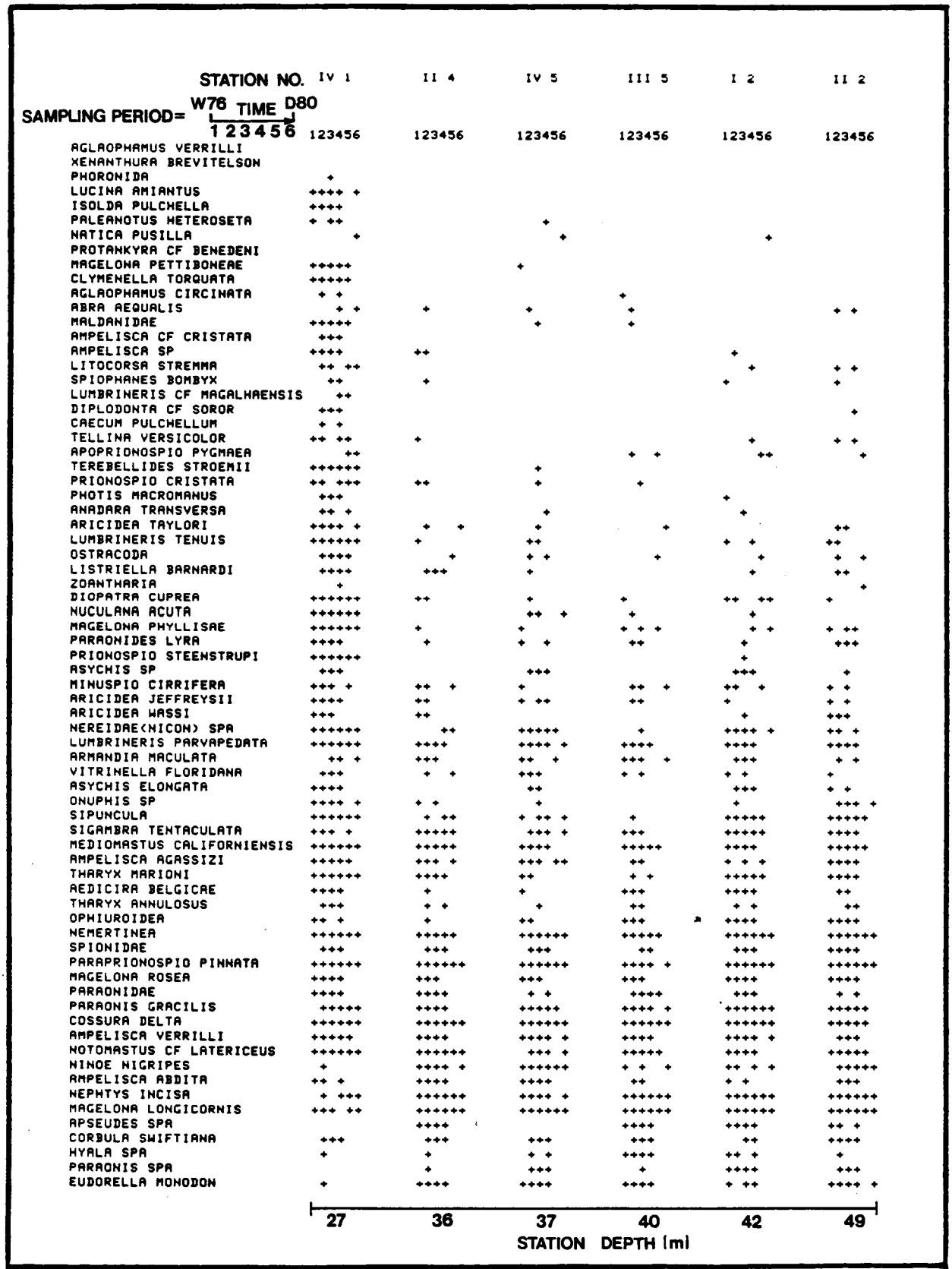


Figure 4-49 (cont'd).

During fall 1976, the sampling period when total abundance and number of taxa observed were highest, most taxa which were present spanned the entire depth range (10-49 m) (Figure 4-48). For example, 40 out of 69 numerically dominant taxa (58%) were present at either or both of the two shallowest stations as well as at either or both of the two deepest stations in fall 1976 (i.e., $\leq$15 m, $\geq$42 m). A relatively large suite of taxa was restricted to the 3 shallowest stations, with an apparent break point between Stations III-4 and IV-4 (depth 15 m) and Station I-1 (depth 18 m) (Figures 4-48 and 4-49). However, one of the deeper stations (IV-1, depth 27 m) showed a very similar pattern to the three shallowest stations. Taken as a group, 15 taxa (22% of 69) were found at these four stations and no others during this sampling period. All four stations were characterized by fairly coarse, sandy sediment. At the other end of the scale, three taxa found primarily at the deeper stations (the gastropod Hyala sp. A, the paraonid polychaete Paraonis sp. A, and the cumacean Eudorella monodon) were rare or absent from the shallowest stations.

In winter 1977, the sampling period when total abundance and number of taxa observed were second highest, a similar picture was seen. Thirty-three out of 68 numerically dominant taxa present (49%) spanned the depth range from either or both of the two shallowest stations to either or both of the two deepest stations. Eleven of the 68 numerically dominant taxa (16%) were restricted to the group of four sandy-sediment stations mentioned above (depth 27 m or less). One of the taxa present only at the deepest stations in fall 1976 (Paraonis sp. A) was found at the shallowest station (I-4) in winter 1977.

During fall 1977, when total abundance and number of taxa observed were third highest, several changes were evident in Figure 4-48. Thirty-eight out of 69 numerically abundant taxa (55%) were present over the broad depth range from $\leq$15 m to $\geq$42 m. However, a number of taxa that were formerly present at all stations (nine in fall 1976, eleven in winter 1977) were reduced in distribution (five in fall 1977) or even completely absent (the paraonid polychaete Aricidea wassi). In the case of these taxa which were relatively non-depth-specific, stations at middle depths were as likely to be deleted from the distribution as those at either end of the depth range. Nineteen out of 69 numerically abundant taxa (28%) were restricted to the four sandy stations mentioned above. Only two taxa (Hyala sp. A and Eudorella monodon) were still absent from the shallowest stations.

During winter 1976, total abundance and number of taxa observed were third lowest. Perhaps the most obvious difference was that a number of taxa which (on the basis of the data from fall 1976 and winter 1977) have potentially wider habitat preferences were restricted in their distribution. Twenty-five out of 65 numerically dominant taxa (38%) spanned the depth range from $\leq$15 m to $\geq$42 m. Only three taxa were present at all twelve stations, the third lowest value recorded. Twelve out of 65 numerically dominant taxa (18%) were present only at the four sandy stations. Three taxa (the pelecypod Corbula swiftiana, Hyala sp. A, and Paraonis sp. A) were found only at the three deepest stations.

The samples from 1979 and 1980 appear in Figure 4-48 to be markedly different from those taken in all previous sampling periods. The numbers of numerically dominant taxa dropped to 47 and 41, respectively. Losses were present in shallow, deep, and non-depth-specific taxa. Seventeen out of 47 taxa (36%) spanned the depth range from $\leq$15 m to $\geq$42 m in 1979, and eleven out of 41 taxa (27%) in 1980. However, in both years, only a single taxon was present at all 12 stations (Nemertinea in 1979, Paraprionospio pinnata in 1980). Seventeen out of 47 taxa (36%) were restricted to the set of four sandy stations in 1979; in 1980, ten out of 41 taxa (24%) were similarly limited in distribution.

Conspicuous absences from the 1979 and/or 1980 samples included the polychaetes Paleanotus heteroseta (Palmyridae), Aricidea jeffreysii, Aricidea wassi, Paraonides lyra, Paraonis sp. A and Aedicira belgicae (Paraonidae), Tharyx annulosus (Cirratulidae), Magelona rosea (Magelonidae), Aglaophamus circinata (Nephthyidae), Asychis sp., Asychis elongata (Maldanidae); the gastropods Hyala sp. A and Caecum pulchellum; the pelecypods Anadara transversa, Corbula swiftiana, Diplodonta cf. soror and Tellina versicolor; the corophiid amphipod Photis macromanus; the ampeliscid amphipods Ampelisca abdita, Ampelisca cf. cristata and Ampelisca sp.; the tanaid Apseudes sp. A; the cumacean Eudorella monodon; and miscellaneous unidentified spionid polychaetes, ophiuroids, phoronids, and zoantharians.

Figure 4-49 graphically illustrates a decrease in the number of taxa with increasing depth. Many taxa present in shallow water were very scarce or absent at stations deeper than 15 m deep. The notable exception to this generalization is the fauna of Station IV-1 (27 m), which has a set of shallow-water taxa similar to that at the three shallowest stations, as mentioned above. The inverse is not true; only three taxa (Hyala sp. A, Paraonis sp. A, and Eudorella monodon) were rarely found at the shallowest stations. Other than these, no clearly defined set of taxa was associated with the deeper stations. The great majority of taxa common at the deepest stations were also as likely to be present at the shallowest stations.

Figures 4-50 and 4-51 summarize the cumulative numbers (4-50) and relative proportions (4-51) of taxa which occurred at a given number of stations within each sampling period. The percentages given in Figure 4-51 accumulate horizontally to 100%, and are thus independent of the total numbers of taxa present within any given sampling period. The data show that in fall 1976, a higher proportion of taxa (68%) appeared at more than one station than in any other sampling period, followed by fall 1977 (66%), winter 1977 (60%), 1979 (58%), and winter 1976 and 1980 (both 57%). Periodic trends are not obvious in the data for multiple occurrences at fewer than three or four stations, indicating that most taxa found in any sampling period were present at at least a few sites. Despite this similarity between sampling periods for low levels of multiple occurrences, the highest percentage of multiple occurrences at nearly every level from two or more stations through twelve was seen in fall 1976; in other words, a greater proportion of taxa appeared at more stations during fall 1976 than during any other sampling period.

At higher levels of multiple occurrences, differences between sampling periods were more evident, based upon the median value for multiple occurrences (i.e., the percentage of taxa which were present at seven or

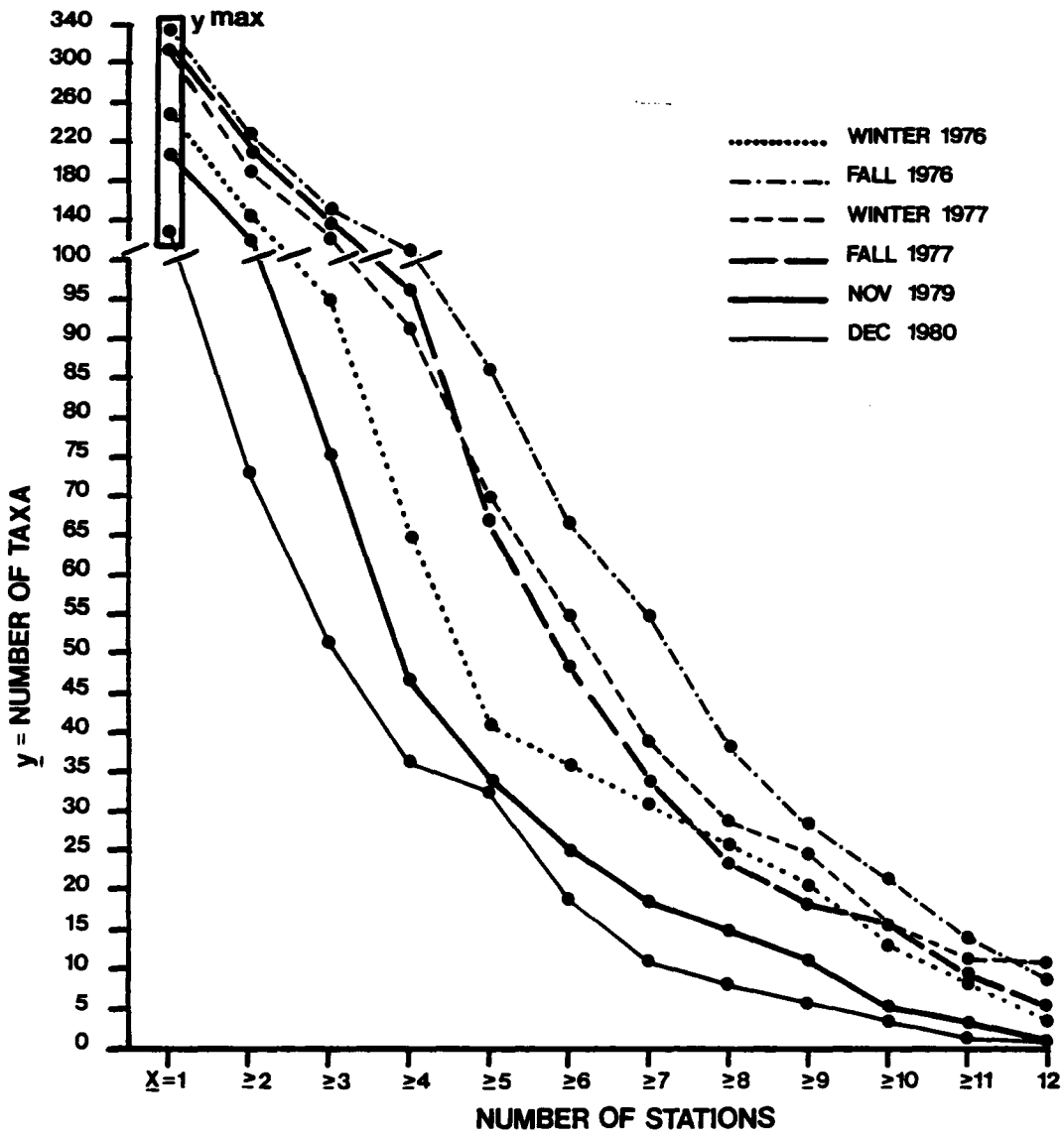


Figure 4-50. Numbers of taxa (y) at a given number of stations (x), by sampling period (y max = total number of taxa per sampling period).

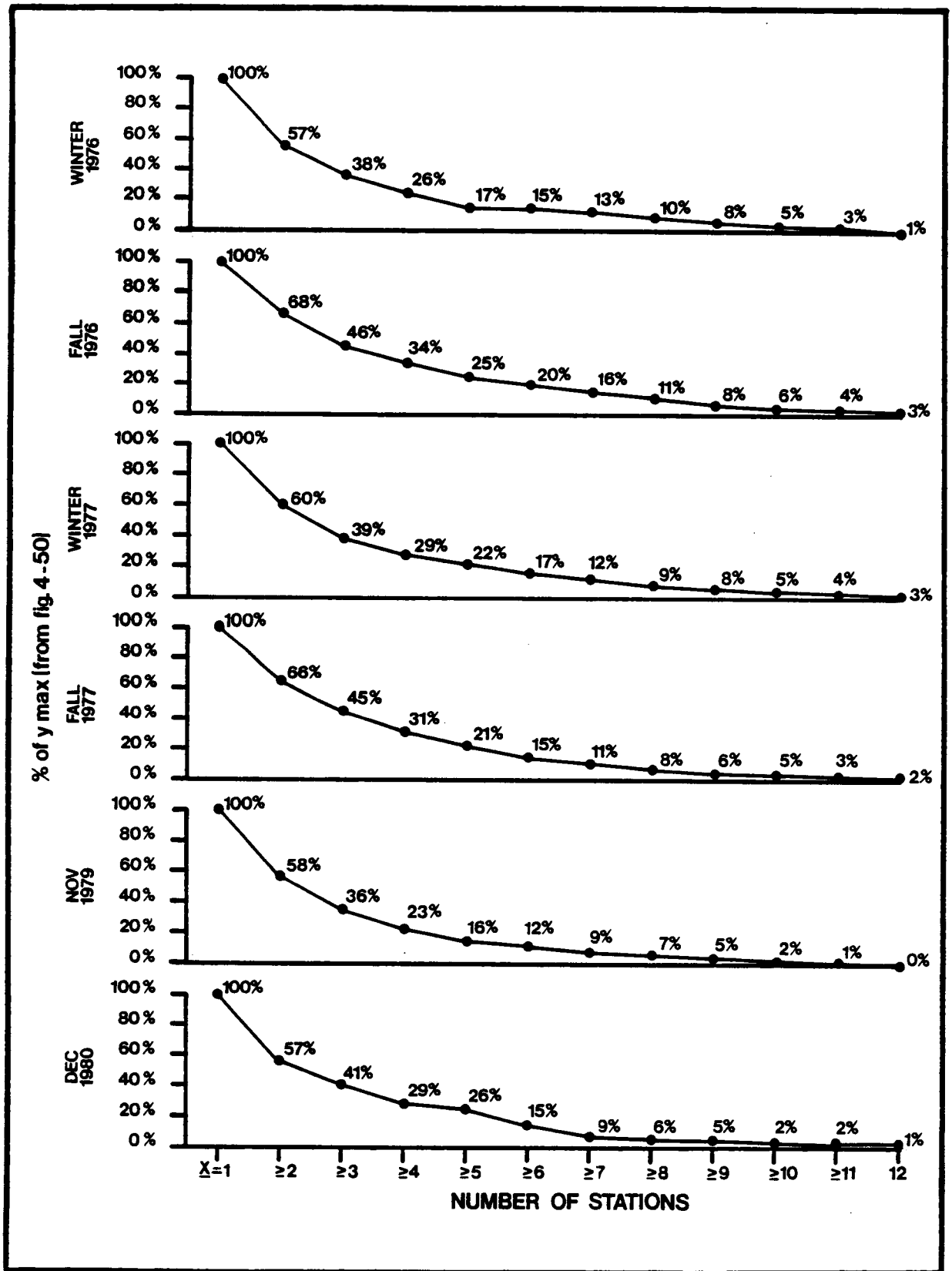


Figure 4-51. Relative proportions of numbers of taxa (% of y max from Figure 4-50) at a given number of stations, by sampling period.

more stations). In winter 1976, the median value was 13%. In fall 1976, the median value rose to 16%. From winter 1977 onward, the median value for multiple occurrences dropped steadily from 12% to 11% a low of 9%, indicating a progressively narrower range of habitat availability for taxa which previously had been very widely distributed.

Relatively clear patterns of association between stations were produced for each sampling period by cluster analysis based upon abundance of numerically dominant taxa and then inverted to group stations (Figures 4-52 through 4-58). Stations were generally clustered into three major groups by use of a distance measure of 0.80 as a defining limit: three nearshore and one deeper station (I-4, III-4, IV-4, and IV-1); five offshore stations (I-2, II-4, II-2, III-5, and IV-5), and three lying at some intermediate distance (I-1, II-1, and III-1). At a higher level (distance measure 0.85-0.91), stations were grouped into two clusters, a nearshore assemblage usually including just the inshore group previously delimited by the 0.80 distance measure, and an offshore assemblage usually including the members of the offshore and intermediate groups that had been separated by the 0.80 distance measure. Unless otherwise mentioned, all text references to groupings in cluster analyses by individual sampling periods are based upon use of the 0.80 distance measure.

When samples from fall 1976 were clustered with those from winter 1977 (the two samples taken closest together in time), in eight out of twelve stations the most closely associated groupings were the paired fall and winter samples from the same station (Figure 4-55) although four stations did not show this tendency (indicated by stars on Figure 4-55). This observation is in accord with the results presented in the trellis diagram (Figure 4-8), which showed the strongest associations between these two sampling periods.

A two-way table for all stations and sampling periods was produced by merging the cluster analysis based upon abundance of numerically dominant taxa with an inverse dendrogram by station and time period, regarding each sampling period at each station as a separate entity. The 72 station-period x 72 taxa matrix itself is not reproduced in this report due to its size (reduction to the proper format made it wholly illegible) but the two cluster groupings (Station Groups and Animal Groups) resulting from the analysis are presented in Figure 4-59. A copy of the original matrix is available on request from the senior author (G.S. Lewbel).

At least four major groups of station/periods (numbered Station Groups 1-4) emerged, while the pattern by taxa was much more complicated and was divided into nine lettered Animal Groups (A-I). In interpreting the results, the reader should keep in mind that a Station Group may have included several stations sampled at the same or at different times, and/or the same station sampled at different times. The same stations did not always appear in the same cluster through time, indicating substantial heterogeneity in taxonomic composition within stations from one sampling period to the next. Individual Station Groups are broken out in more detail in Figures 4-60 through 4-63.

Station Group 1 included a set of stations ranging in depth from 25 m to 49 m (average depth 38 m), primarily having fairly fine silty-clay sediment (Figure 4-60). These six offshore stations were biologically

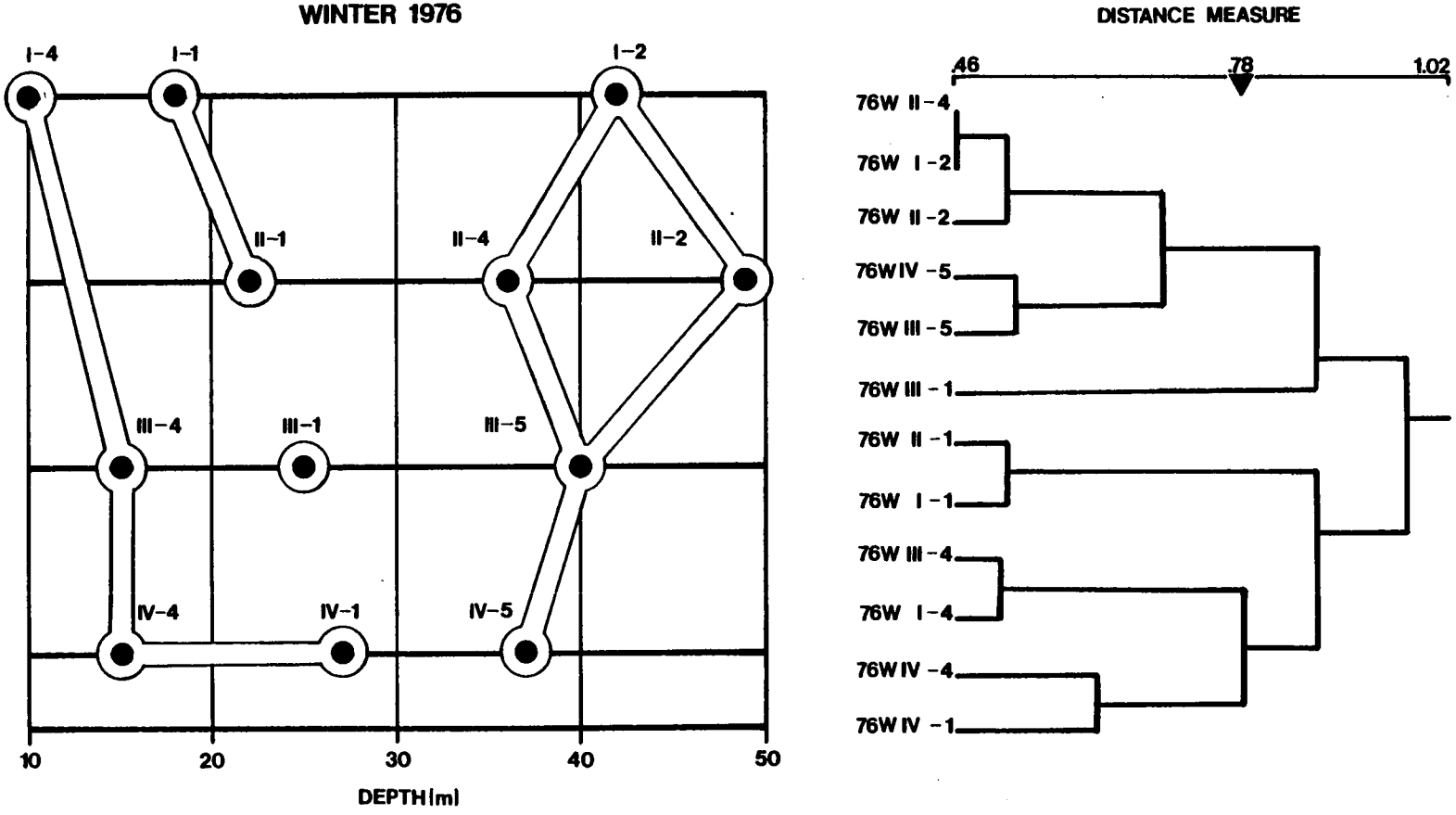


Figure 4-52. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for winter 1976 (0.2% cutoff).

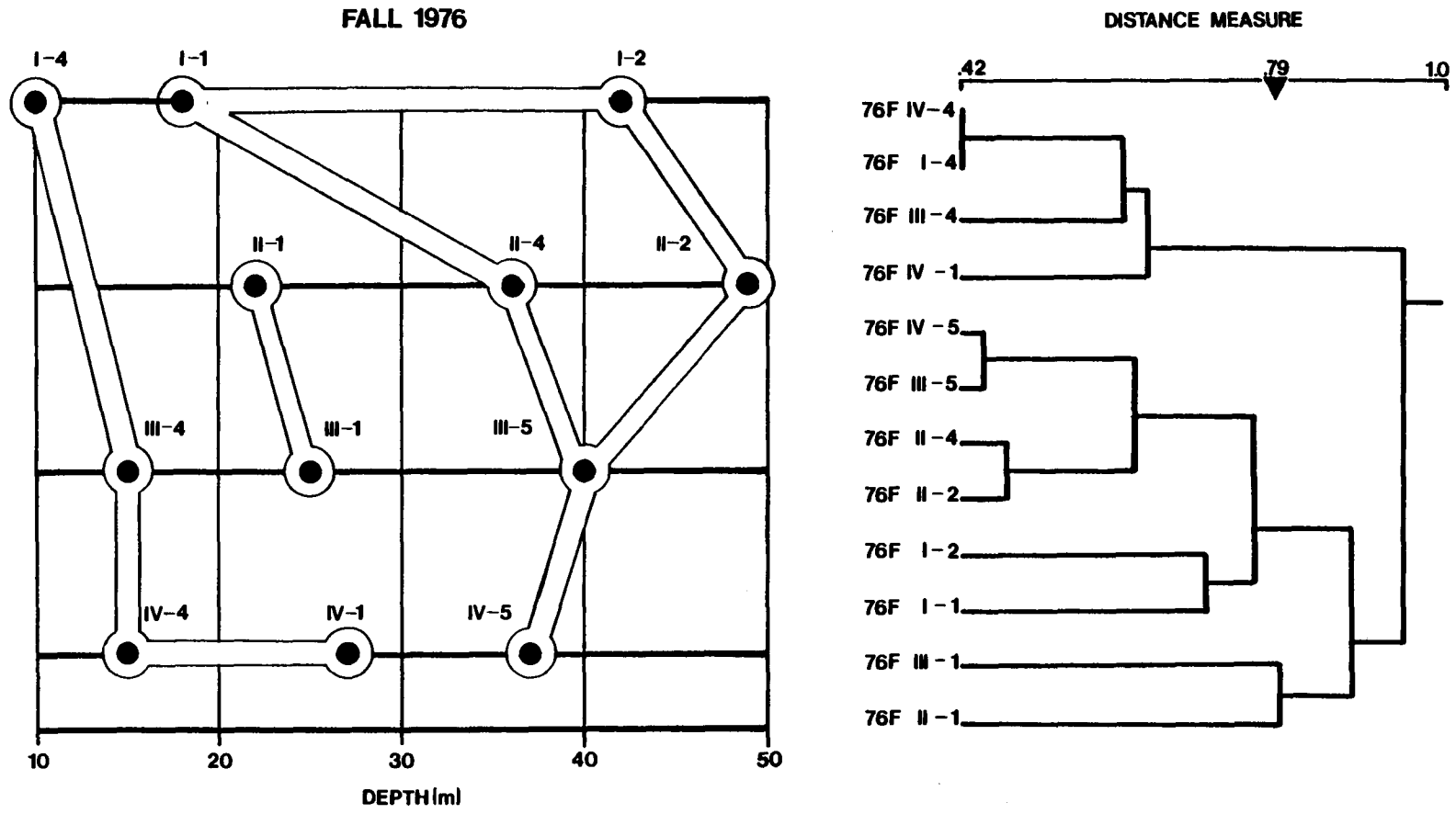


Figure 4-53. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for fall 1976 (0.2% cutoff).

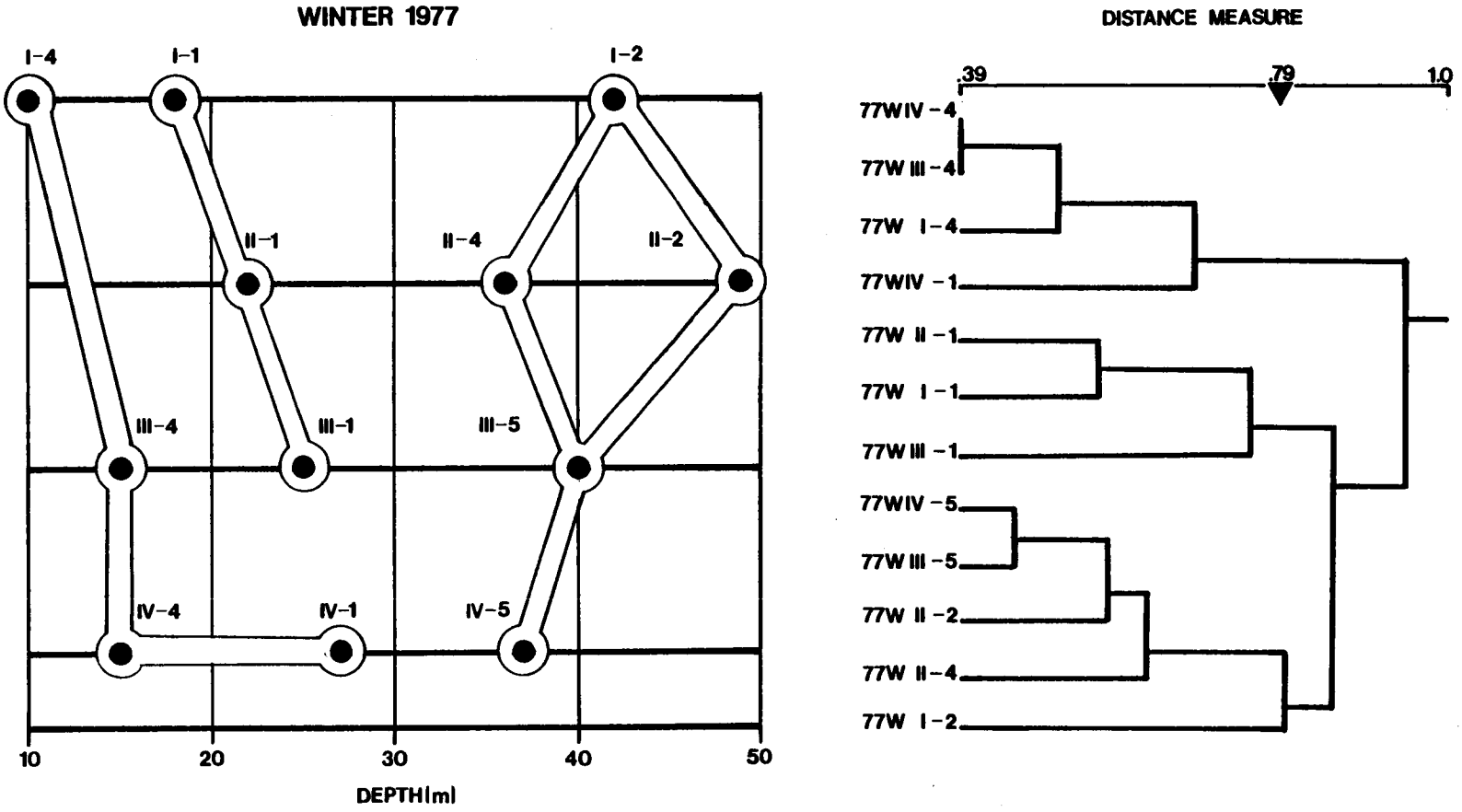


Figure 4-54. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for winter 1977 (0.2% cutoff).

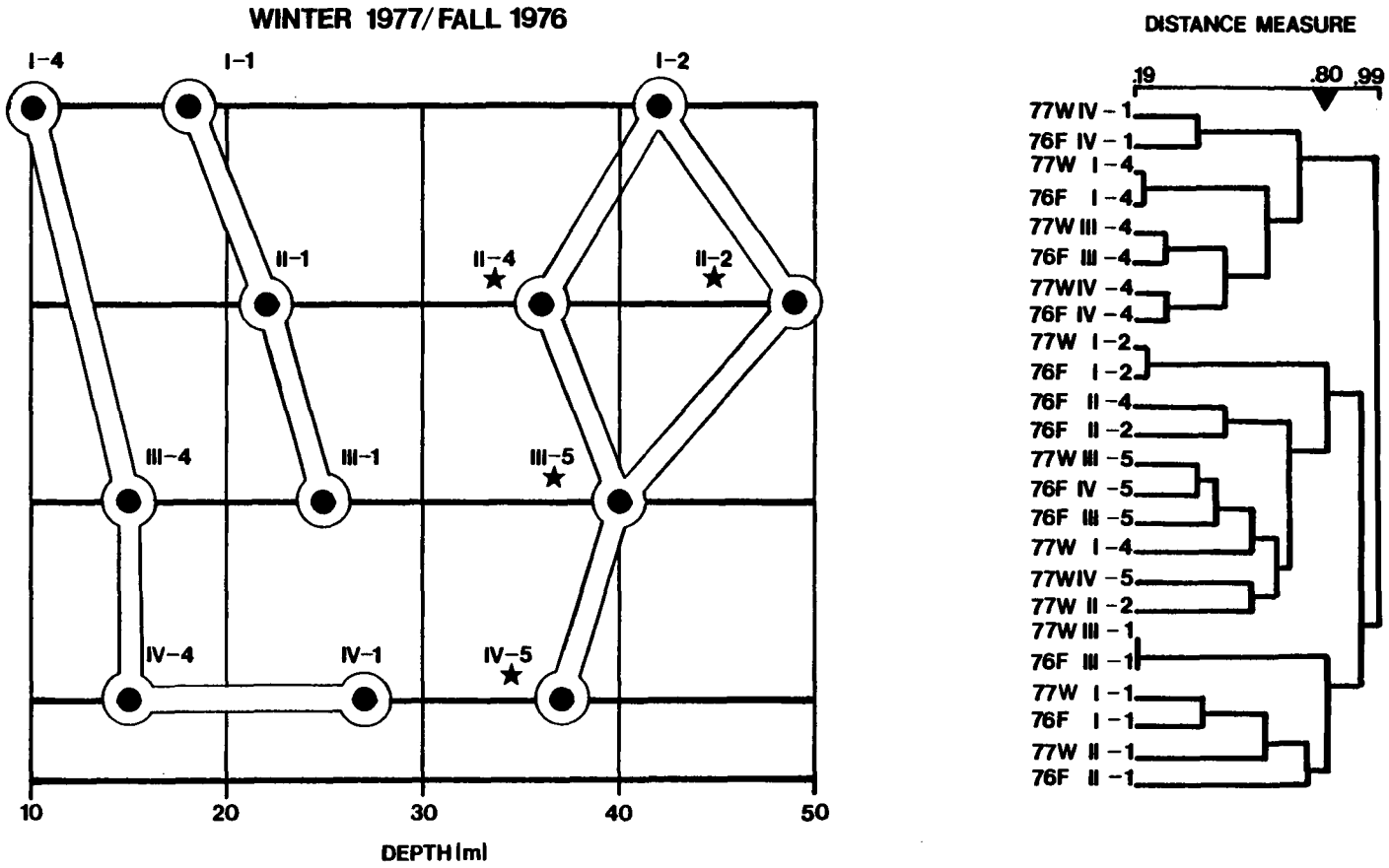


Figure 4-55. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for fall 1976 and winter 1977 together. Stars indicate stations at which fall 1976 and winter 1977 samples did not cluster most closely, i.e. pairwise (see text for explanation) (0.2% cutoff).

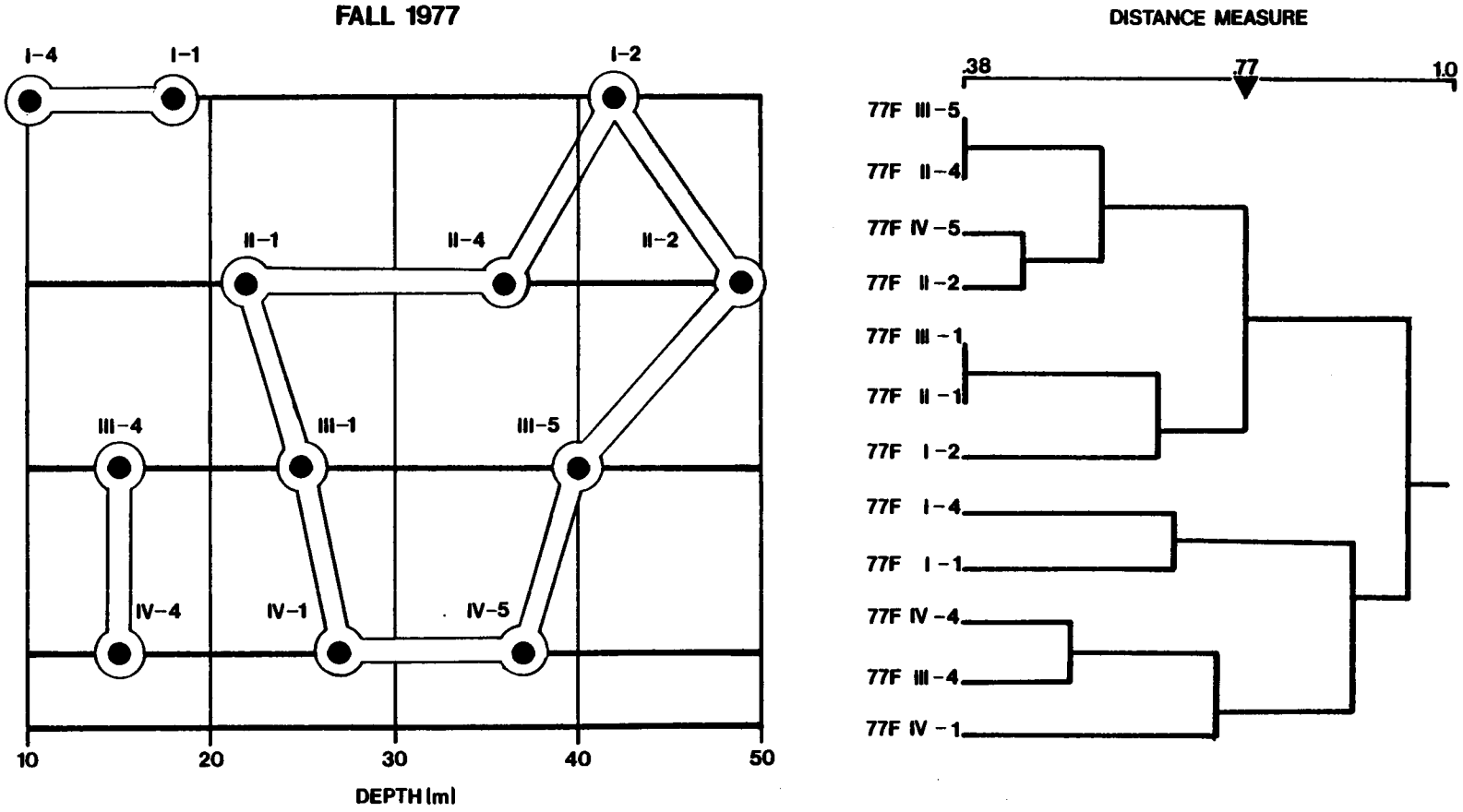


Figure 4-56. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for fall 1977 (0.2% cutoff).

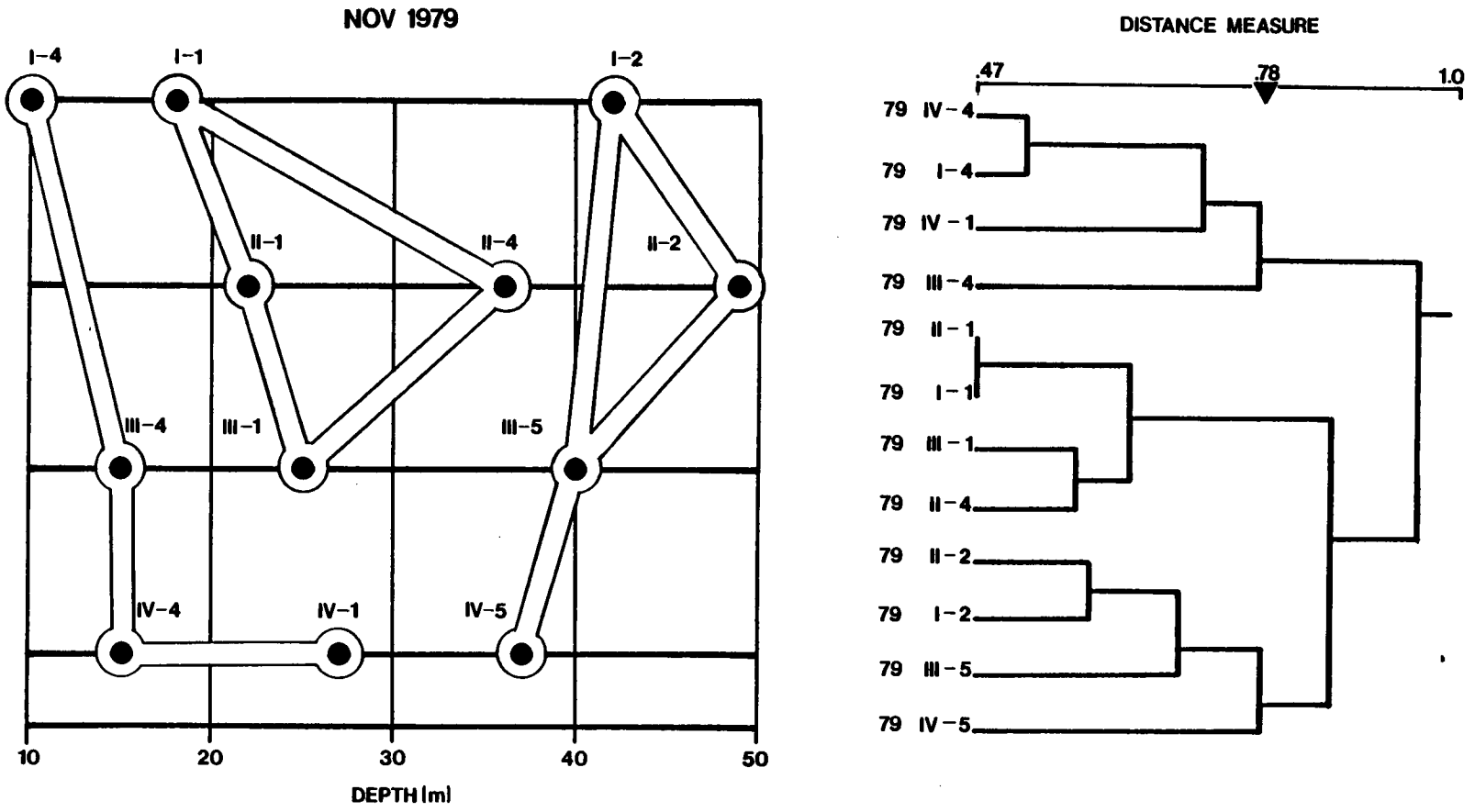


Figure 4-57. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for 1979 (0.2% cutoff).

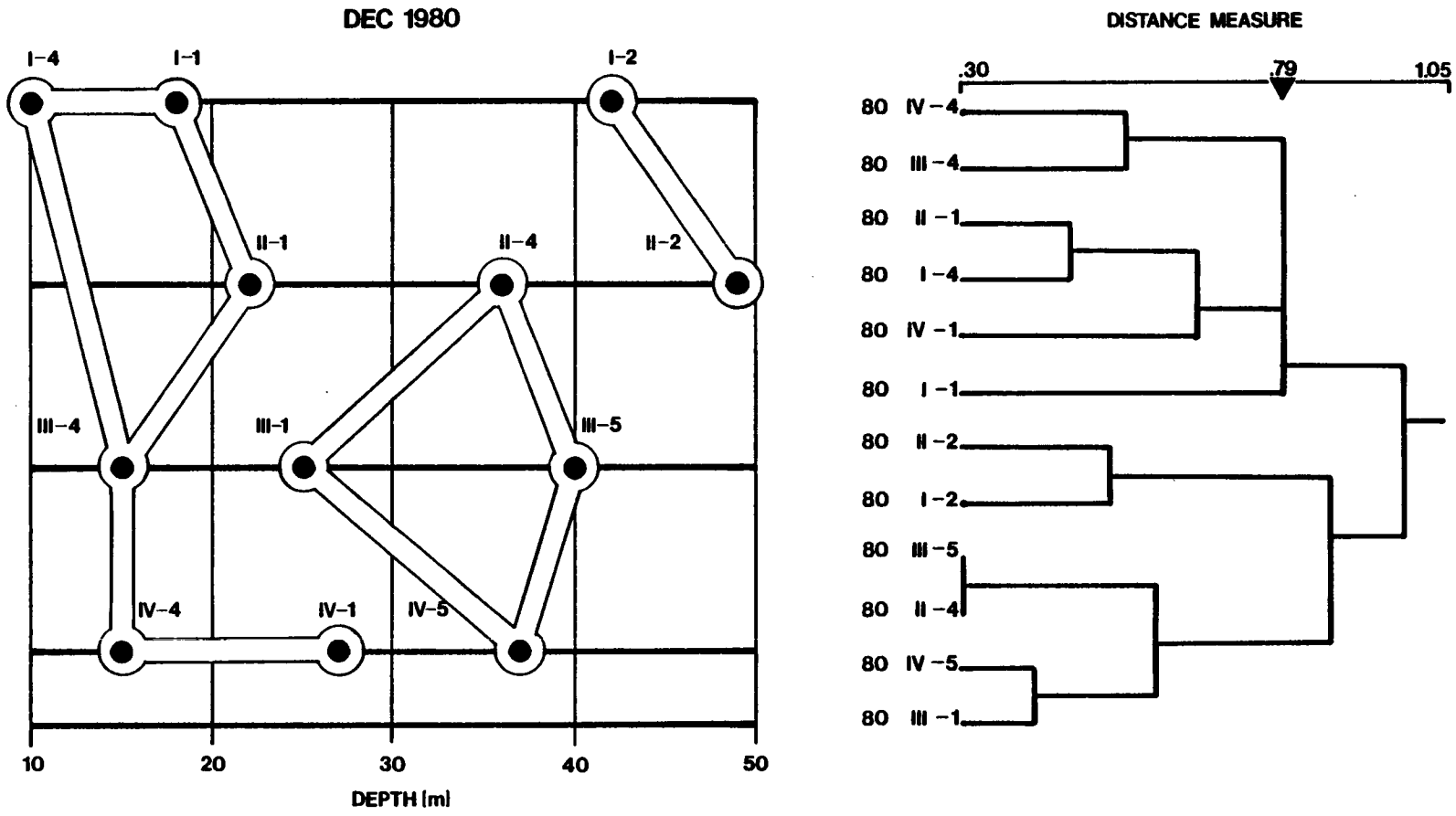


Figure 4-58. Schematic map of station groupings derived from cluster analysis of abundance of numerically dominant taxa, for 1980 (0.2% cutoff).

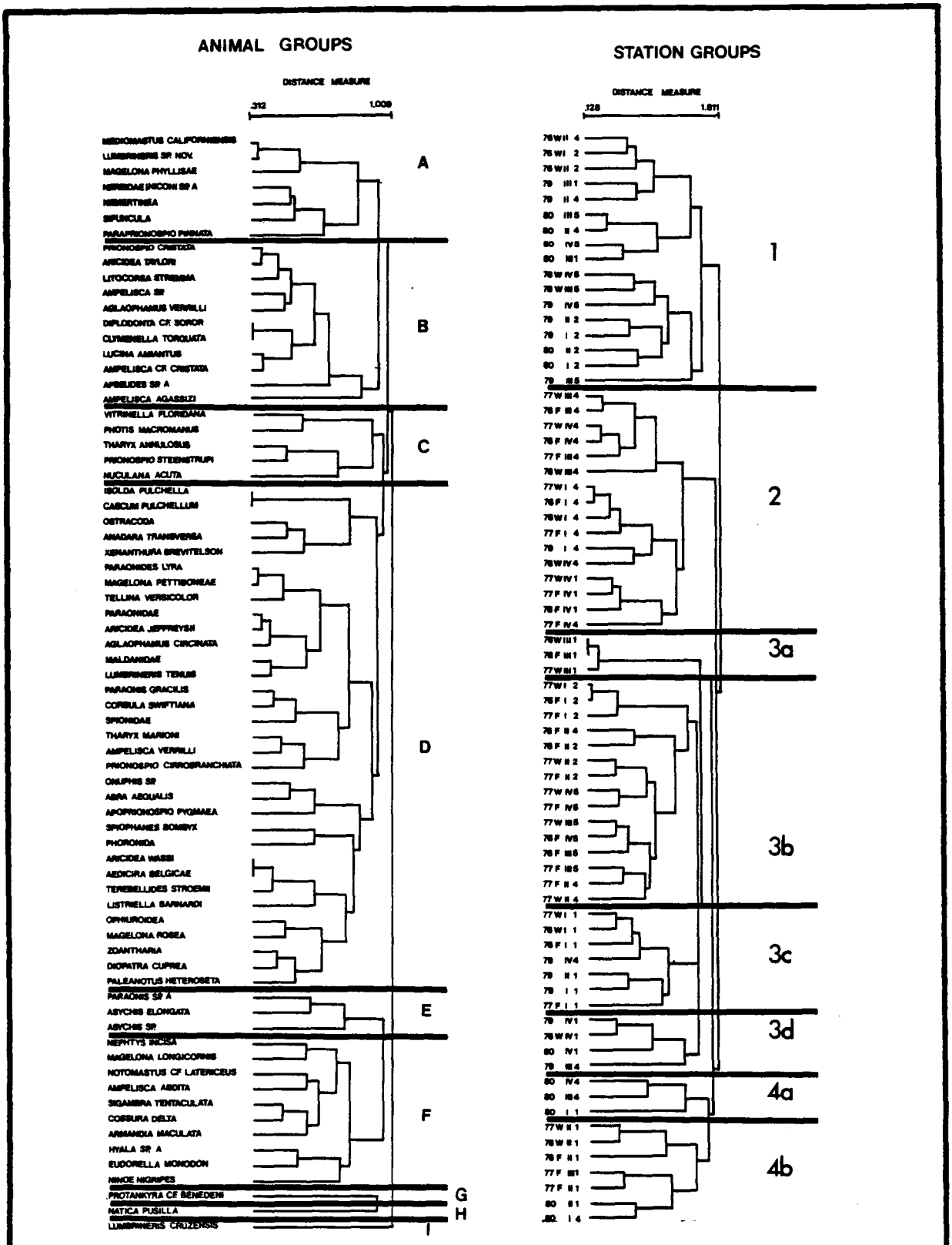


Figure 4-59. Animal Groups (left) and Station Groups (right) derived from cluster analyses (see text for explanation) (0.2% cutoff).

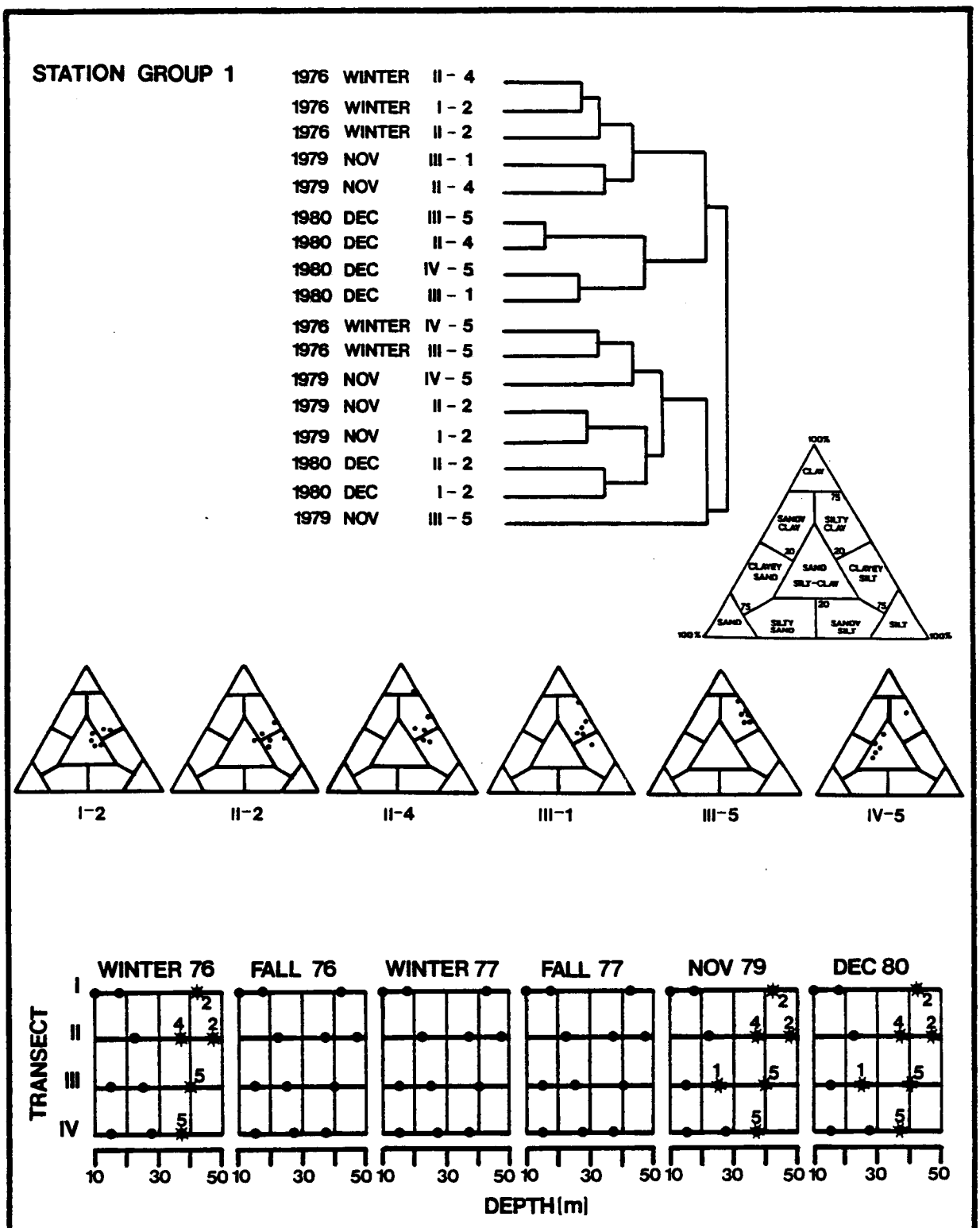


Figure 4-60. Station Group 1 (from Figure 4-59); station numbers and sampling periods are shown in cluster diagram (top) and on schematic location grids (asterisks, bottom); sediment profiles for each station (center) include six sampling periods (dots) for comparison (see text for explanation).

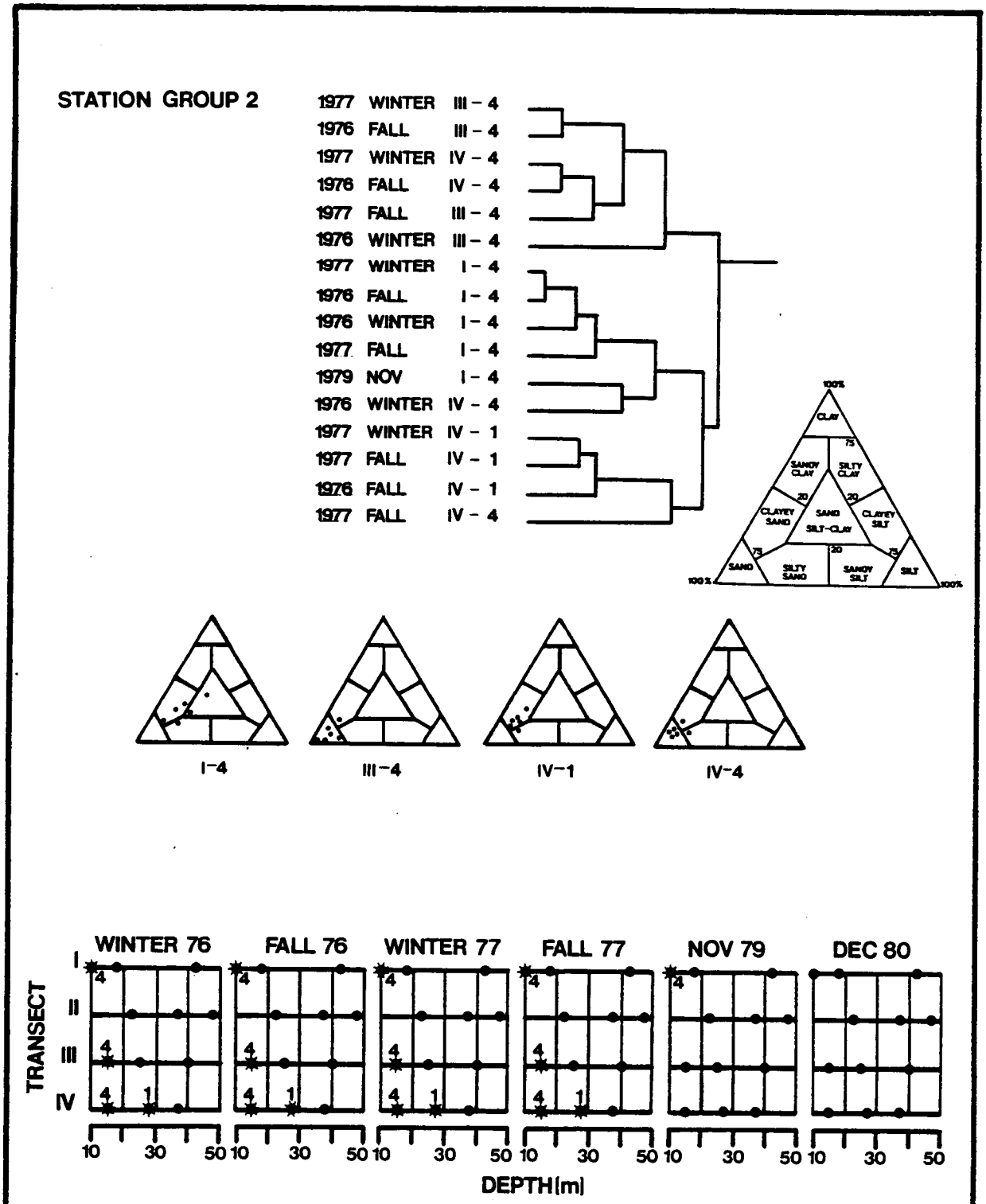


Figure 4-61. Station Group 2 (from Figure 4-59); station numbers and sampling periods are shown in cluster diagram (top) and on schematic location grids (asterisks, bottom); sediment profiles for each station (center) include six sampling periods (dots) for comparison (see text for explanation).

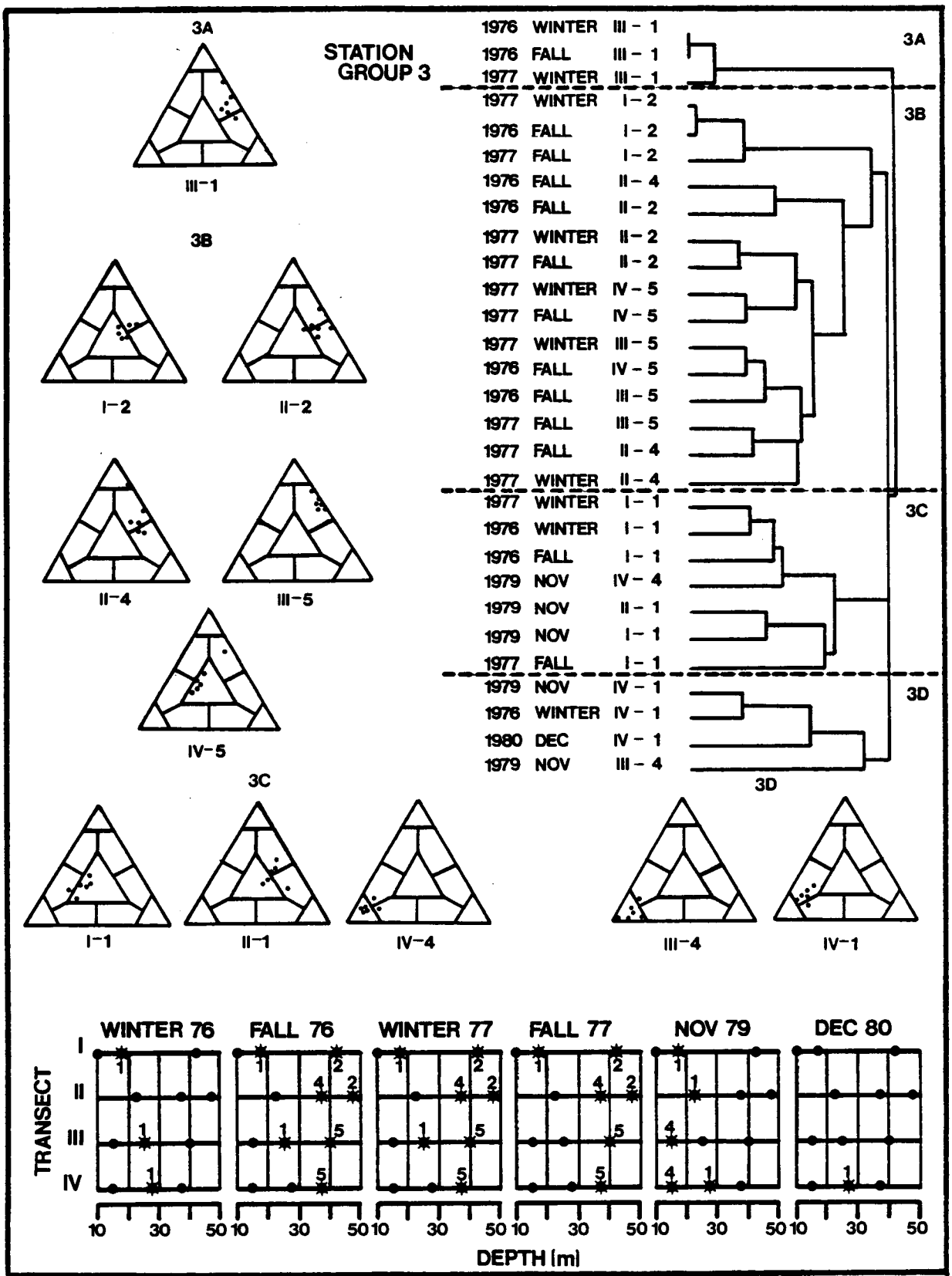


Figure 4-62. Station Group 3 (from Figure 4-59); station numbers and sampling periods are shown in cluster diagram (top) and on schematic location grids (asterisks, bottom); sediment profiles for each station (center) include six sampling periods (dots) for comparison (see text for explanation).

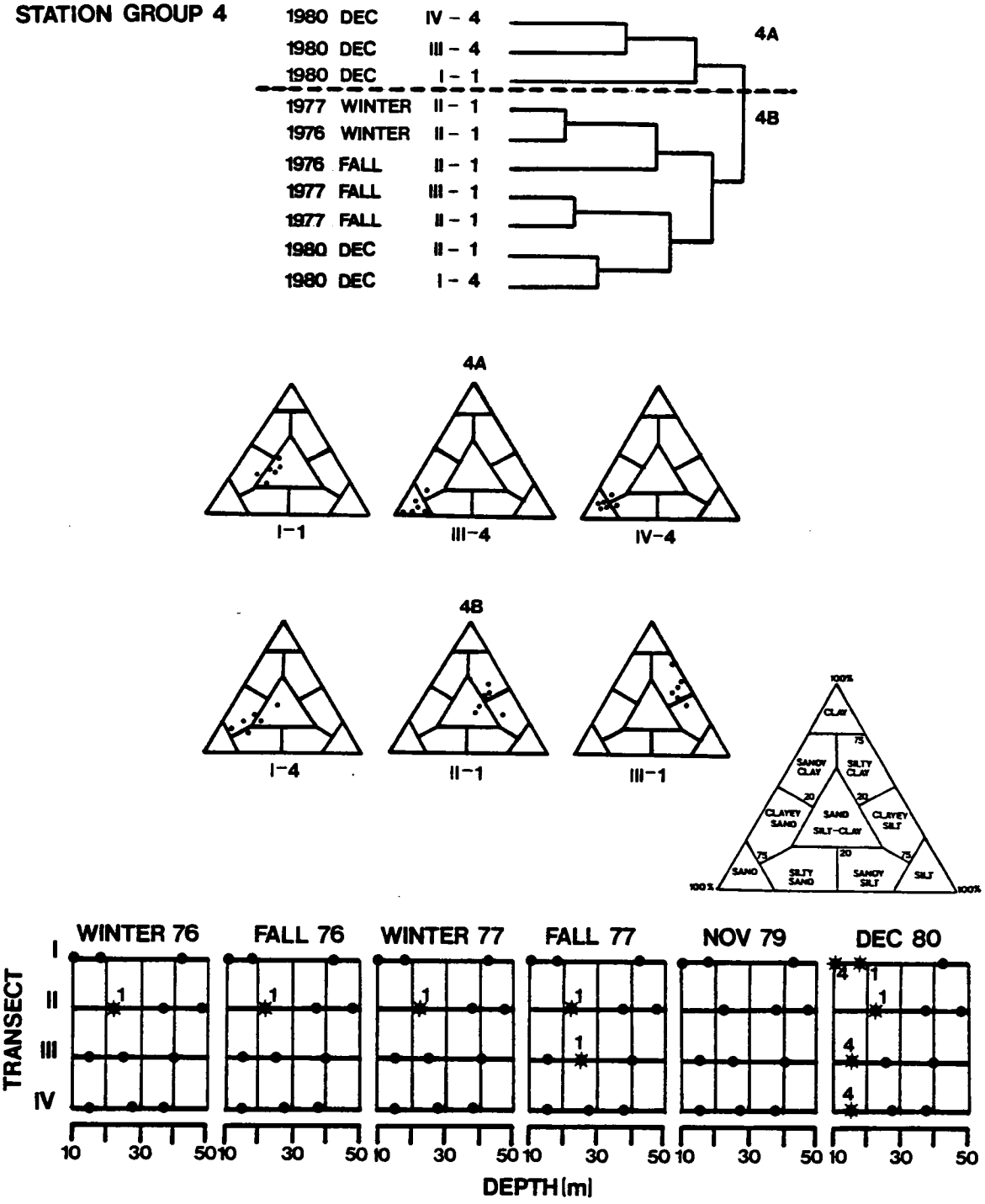


Figure 4-63. Station Group 4 (from Figure 4-59); station numbers and sampling periods are shown in cluster diagram (top) and on schematic location grids (asterisks, bottom); sediment profiles for each station (center) include six sampling periods (dots) for comparison (see text for explanation).

most similar to one another in winter 1976, and in 1979 and 1980; none of the fall 1976, winter 1977, or fall 1977 samples were within Station Group 1. This association may be also be seen clearly in Figure 4-52, as the winter 1976 offshore cluster of six stations included five from Station Group 1. In Figure 4-57, all four of the 1979 offshore cluster of stations and two of the intermediate cluster of stations were included in Group 1. In Figure 4-58, all six of the stations falling within the 1980 offshore and intermediate clusters of stations were included within Station Group 1.

Station Group 1 included 51 dominant taxa, made up primarily of organisms in Animal Groups A and F. Numerically important forms included the polychaetes Paraprionospio pinnata, Nephtys incisa, and Magelona longicornis; the amphipod Ampelisca agassizi; and unidentified species of nemerteans and ostracods. Compared to the other three major station groupings, Station Group 1 had relatively few of the numerically dominant taxa per station/period (mean = 16, standard deviation = 8.0, range = 7-30). Diversity (H') and evenness (V') for 51 numerically dominant taxa were 3.10 and 0.77, respectively, for Station Group 1. When no cutoff limits were used, H' and V' were 3.83 and 0.72, respectively, based upon data from 153 taxa.

Station Group 2 included a set of stations (I-4, III-4, IV-4, and IV-1) ranging in depth from 10 m to 27 m (average depth 17 m), primarily having coarse sandy and clayey-sand sediment (Figure 4-61). Three of these are shallow nearshore stations (depth range 10-15 m), while the fourth is somewhat deeper (27 m). As a group, they are the same stations discussed above as being sandy and containing virtually all of the taxa which were absent at the remaining eight stations (Figure 4-49). The stations were biologically most similar to one another during 1976 and 1977. They may also be seen in Figure 4-52 as all four of the winter 1976 nearshore cluster of stations; in Figure 4-53 as three of the four fall 1976 nearshore cluster of stations; in Figure 4-54 as all four of the winter 1977 nearshore cluster of stations; and in Figure 4-56 again as all four of the fall 1977 nearshore cluster of stations. In 1979, only the shallowest of the stations in Group 2 (Station I-4, depth 10 m) remained within the Group as a single element, now part of the four-station nearshore cluster (Figure 4-57).

Station Group 2 included 71 of the 72 numerically dominant taxa, and was characterized by the presence of most of the taxa in nearly every station/period (mean = 43, standard deviation = 19, range = 29-64). The only consistently abundant taxon was the polychaete Magelona phyllisae, though miscellaneous unidentified sipunculids were represented in large numbers in a single sample from station I-4 in fall 1977. Diversity (H') and evenness (V') for 71 numerically dominant taxa were 3.29 and 0.77, respectively, for Station Group 2. When no cutoff limits were used, H' and V' were 3.91 and 0.63, respectively, based upon 463 taxa.

Station Group 3 was a heterogeneous assemblage of mostly offshore and intermediate stations having silty-clay sediment, biologically similar to one another during 1976 and 1977, and a set of inshore stations having more sandy sediment and resembling the other deeper stations primarily in 1979 (Figure 4-62). Station Group 3 was further subdivided into four subgroups (3a, 3b, 3c, and 3d) due to the mixture of sediment types present, and the

apparently anomalous grouping of deep water stations with nearshore stations.

Station Group 3a included only Station III-1 (depth 25 m), which has fine silty-clay sediment, and which was dominated from winter 1976 through winter 1977 by the amphipod Ampelisca agassizi. During this period the taxonomic composition of the station remained quite constant in terms of numbers of numerically dominant taxa per station/period (mean = 31, standard deviation = 3.1, range = 28-34). Organisms from Animal Groups A and F were well represented in Station Group 3a, also. Station III-1 may be seen in Figure 4-49 to have had few of the species typical of the nearshore, sandy group, and to share affinities on gross scale with the five deepest stations and with II-1 and I-1, its shallower neighbors, and to have little in common with the next deeper station (IV-1, which resembled the three shallowest stations most closely).

Cluster analyses by individual time periods showed that Station III-1 often had close affinities to two other stations, I-1 (depth 18 m) and II-1 (depth 22 m). In winter 1976 (Figure 4-52) Station III-1 stood alone (although at a higher level of similarity <distance measure 0.86> it grouped with the offshore set of stations, while Stations I-1 and II-1 grouped with the nearshore set of stations, unlike their more typical pattern). In fall 1976 (Figure 4-53), Station III-1 clustered with Station II-1, while in winter 1977 (Figure 4-54) Station III-1 grouped again with Station II-1 and with Station I-1. When the samples from fall 1976 were clustered with those from winter 1977 (Figure 4-55), Station III-1 fall samples grouped most closely with those from Station III-1 winter samples, and were associated again with Stations II-1 and I-1. Diversity (H') and evenness (V') values for 40 numerically dominant taxa were 1.58 and 0.40 for Station Group 3a, respectively. When no cutoff limits were used, H' and V' were 1.82 and 0.37, respectively, based upon 81 taxa.

Group 3b consisted of the five deepest stations (II-4, IV-5, III-5, I-2, and II-2) ranging in depth from 36 m to 49 m (average 41 m), typically having silty-clay sediments. All five of these stations belonged to Station Group 3b throughout the same three sampling periods (fall 1976, winter 1977, and fall 1977). This constancy is also reflected in the individual cluster diagrams by sampling period. In fall 1976 (Figure 4-53), five out of the six offshore stations were from Station Group 3b; the sixth was Station I-1 (depth 18 m), which usually was clustered with the offshore stations rather than with the adjacent nearshore stations due, apparently, to its lack of the suite of species present primarily at the three shallowest station and at Station IV-1 (Figure 4-49). In winter 1977 (Figure 4-54), all five of the offshore cluster of stations were from Station Group 3b. In fall 1977 (Figure 4-56), five out of the seven stations in the offshore cluster were from Station Group 3b.

When the samples from fall 1976 were clustered with the samples from winter 1977 (Figure 4-55), all five of the stations in the offshore cluster were from Station Group 3b. Four of the five stations from Station Group 3b did not show their closest affinities in this cluster analysis between the two consecutive sampling seasons for each station. These four stations (II-2, II-4, III-5, and IV-5) were the only ones out of twelve which did not most closely pair fall and winter samples within stations, indicating

that despite similarities between the Station Group 3b stations, temporal differences were substantial within stations. However, on an overall basis, the fall 1976 and winter 1977 samples from these stations were sufficiently similar to obscure the differences when all station/periods were clustered together.

Numerically dominant species within Station Group 3b included the polychaete Asychis sp., which was abundant from fall 1976 through fall 1977 at Station I-2 (depth 42 m); miscellaneous unidentified spionid polychaetes (common thoughout Station Group 3b but especially abundant in the winter 1977 samples from Station II-2 (depth 49 m); and large numbers of the polychaete Paraprionospio pinnata and miscellaneous unidentified nemerteans in fall 1977. Representatives of Animal Groups A, D, E, and F were also common. Most taxa found in Station Group 3b were those typical of the deeper stations, i.e. those not limited to either deep or shallow stations, but more or less common at all stations; the taxa previously described as typically restricted to shallow and/or sandy environments (e.g. Stations I-4, III-4, IV-4, and IV-1) were rare at Station Group 3b stations. Within Station Group 3b the numbers of numerically dominant taxa were relatively constant (mean = 31, standard deviation = 5.5, range = 17-39). Diversity (H') and evenness values (V') were 3.12 and 0.77, respectively, based upon 57 numerically dominant taxa. When no cutoff limits were used, H' and V' were 3.62 and 0.66, respectively, based upon 205 taxa.

Station Group 3c consisted of three stations of intermediate depth (I-1, IV-1, and II-1, average depth 18 m, range 15-22 m) whose sediment varied from sand to roughly even mixtures of sand, silt, and clay. From winter 1976 through winter 1977 the only component of this group was Station I-1 (depth 18 m). In 1979 Station I-1 was associated with the next deeper Station (II-1, depth 22 m) and the next shallower station (IV-4, depth 15 m).

A clear pattern of shifts in association by Station I-1 back and forth from deeper to shallower groups of stations may be seen in the cluster analyses by sampling period. From winter 1976 through winter 1977, Station I-1 was grouped either with Station II-1 (depth 22 m) or with Station II-1 and Station III-1 (depth 25 m), or with the offshore group of stations in fall 1976 (Figures 4-52, 4-53, and 4-54). At that time it was clearly not a component of the nearshore group of stations (I-4, IV-4, and IV-1) to which its nearest neighbor (Station I-4) belonged. This is also evident from inspection of Figure 4-49. However, in fall 1977 (Figure 4-56), Station I-1 was grouped with its shallow neighbor, Station I-4 (depth 10 m). In 1979, Station I-1 was again clustered with deeper stations, II-1, III-1, and II-4 (depth 36 m) (Figure 4-57). In 1980 (not a period in which Station I-1 was a member of Station Group 3c), Station I-1 was once again associated with the nearshore group of stations (Figure 4-58).

The polychaete Magelona phyllisae dominated the samples from Station Group 3c, although in fall 1977 the polychaete Paraprionospio pinnata and miscellaneous unidentified sipunculids were numerically more important at Station I-1. The most consistent members of Station Group 3c were organisms from Animal Groups A and F. The number of dominant taxa included in the samples from Station Group 3c averaged 28 (standard deviation = 8.0, range 17-40). Diversity (H') and evenness (V') for Station Group 3c were 2.77 and 0.66, respectively, based upon 59 numerically dominant taxa. When

no cutoff limits were used, H' and V' were 3.32 and 0.59, respectively, based upon 191 taxa.

Station Group 3d included only two stations, Station IV-1 (depth 27 m) having fairly coarse clayey-sand sediment, and present in Station Group 3 in winter 1976 and again in 1979 and 1980; and Station III-4 (depth 15 m), which had sandy sediment and was present in Station Group 3 only in 1979. In the cluster analysis by sampling period, Station IV-1 was part of the nearshore group of stations for all three periods (Figures 4-52, 4-57, and 4-58). In the 1979 cluster analysis, Station III-4 was also part of the same nearshore grouping.

None of the numerically dominant taxa present in Station Group 3d was sufficiently abundant to exceed 20% of the total number of individuals in any one station/period. Members of Animal Group A were well represented in Station Group 3d, along with a smattering of other taxa from other groups. Both stations fell within the set of four nearshore and/or sandy stations characterized by the presence of a large number of species absent from the remaining eight stations (Figure 4-49). Number of dominant taxa present averaged 32 (standard deviation = 6.0, range = 27-40). Diversity (H') and evenness (V') for Station Group 3d were 2.26 and 0.81, respectively, based upon 53 numerically dominant taxa. When no cutoff limits were used, H' and V' were 4.14 and 0.75, based upon 195 taxa.

Station Group 4 included six shallow and mid-depth stations (average depth 18 m, range 10-25 m) with shared biological community characteristics during 1976, 1977, and 1980. Station Group 4 is most easily treated as two subgroups, 4a and 4b, each somewhat different in sediment texture and taxonomic composition (Figure 4-62).

Station Group 4a consisted of three shallow stations (IV-4, III-4, and I-1, average depth 16 m, range 15-18 m) which appeared in Station Group 4a only in 1980. In the 1980 cluster analysis (Figure 4-58), the stations of Station Group 4a all were grouped within the nearshore cluster of six stations. Station Group 4a stations had coarse sandy sediment (IV-4 and III-4, both 15-m deep) and somewhat finer silty-clayey sand (I-1, depth 18 m). Dominant taxa in Station Group 4a included the gastropod Natica pusilla (Animal Group H), the polychaete Magelona phyllisae, and the holothuroid Protankyra cf. benedeni (Animal Group G, not seen at any other station at any time). Figures 4-48 and 4-49 further illustrate the situation; in 1980, Stations III-4 and IV-4 lost a large number of typically shallow-water taxa compared to previous periods, thereby closely resembling the pattern at Station I-1, at which of the same taxa had appeared infrequently if at all. Average number of dominant taxa at each station averaged 24 (standard deviation 1.2, range 23-25). Diversity (H') and evenness (V') for Station Group 4a were 2.12 and 0.58, respectively, based upon 38 numerically dominant taxa. When no cutoff limits were used, H' and V' were 2.82 and 0.57, respectively, based upon 101 taxa.

Station Group 4b included two stations of intermediate depth (II-1, depth 22 m, and III-1, depth 25 m) and one shallow station (I-4, depth 10 m). Station II-1 had fairly fine silty-clay sediment, and was represented consistently in Station Group 4b during all four 1976 and 1977 sampling periods and in 1980. Station III-1 also had fine silty-clay sediment, and was a component of Station Group 4b only once (fall 1977). The shallower

station (I-4) joined the others in Station Group 4b only in 1980. In 1980, Station I-4 lost many shallow-water associated taxa, thus coming to resemble the deeper stations more closely, since most of the taxa found at deeper stations were also common in shallow water (Figures 4-48 and 4-49). A somewhat similar pattern may be seen in the individual cluster analyses by sampling period. In winter 1976, fall 1976, and winter 1977, Station II-1 was most closely associated with either two stations of intermediate depth (III-1 and I-1, depths 18 and 25 m respectively) or with the offshore cluster of stations (Figures 4-52, 4-53, and 4-54). When fall 1976 and winter 1977 samples were clustered together (Figure 4-55), Station Group 4b stations were associated with Station I-1. Both Station Group 4b stations present in fall 1977 were clustered with the offshore group (Figure 4-56). In 1980, Station II-1 was grouped with the nearshore, shallow group of stations (unlike previous associations) of which Station I-4 was also a member (Figure 4-58).

Dominant taxa in Station Group 4b were the polychaetes Paraprionospio pinnata, Magelona phyllisae, and Mediomastus californiensis, the gastropod Natica pusilla, and the amphipod Ampelisca agassizi. Taxa from Animal Groups A and F were consistently represented in Station Group 4b. An average of 24 of the 72 numerically dominant taxa were present within each station/period (standard deviation = 5.6, range 15-35). Diversity (H') and evenness (V') for Station Group 4b were 2.36 and 0.59, respectively, based on 38 numerically dominant taxa. When no cutoff limits were used, H' and V' were 2.67 and 0.53, respectively, based upon 124 taxa.

The relative importance of the various Animal Groups (A-I) delineated by the cluster analyses did not remain constant with time, although some general patterns were evident (Figures 4-64, 4-65, and 4-66). They will be treated below in approximate order of overall abundance. Numerically dominant taxa only (0.2% cutoff) are included. The percentages in Figure 4-65 sum vertically to 100%, and thus represent the relative abundance of each group within individual sampling periods.

Animal Group A included only seven taxa but was represented by more individuals (29,262) than any other group in every sampling period, from 49% to 62% of all individuals collected. All seven taxa were present in all sampling periods. The number of individuals per taxon in Animal Group A was higher than in any other group in every sampling period but 1980, when high densities of Natica pusilla (Animal Group H) at three stations and Protankyra cf. benedeni (Animal Group G) at one station raised the number of individuals per taxon above the value for Animal Group A. Animal Group A had its highest abundance per taxon in fall 1976 (1,186), followed by a slight decline in winter 1977 (1,033) and a greater drop in fall 1977 (877). The winter 1976 value (635) was about half that in fall 1976, and 1979 (266) and 1980 (183) values were about a fifth of those in fall 1976. Animal Group A included three deposit feeding polychaetes (Paraprionospio pinnata, Mediomastus californiensis, and Magelona phyllisae), two carnivorous or omnivorous polychaetes (Lumbrineris sp. nov. and Nereis micromma), and two taxa not differentiated beyond the phylum level (the carnivorous nemerteans and the deposit feeding sipunculids).

Animal Group D included 33 taxa, comprised of a variety of feeding types; all were present in fall 1976, while 32 were present in winter 1976,

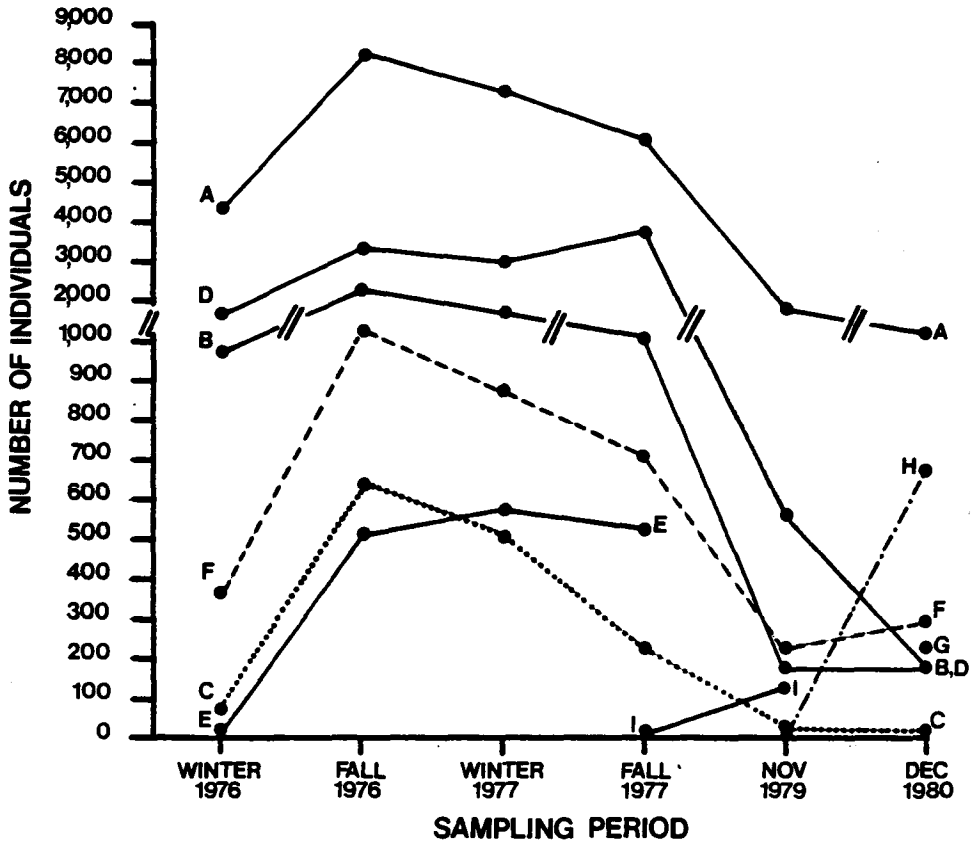


Figure 4-64. Numbers of individual Animal Cluster Groups A through I (from figure 4-59), by sampling period.

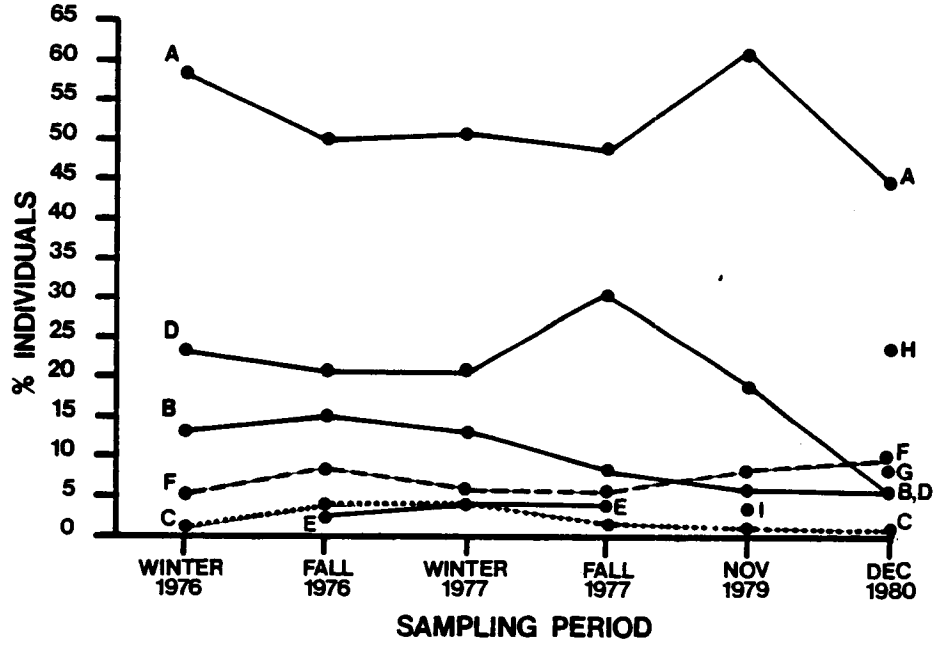


Figure 4-65. Relative proportions of numbers of individuals of Animal Cluster Groups A through I (from Figure 4-59), as % of total within each sampling period.

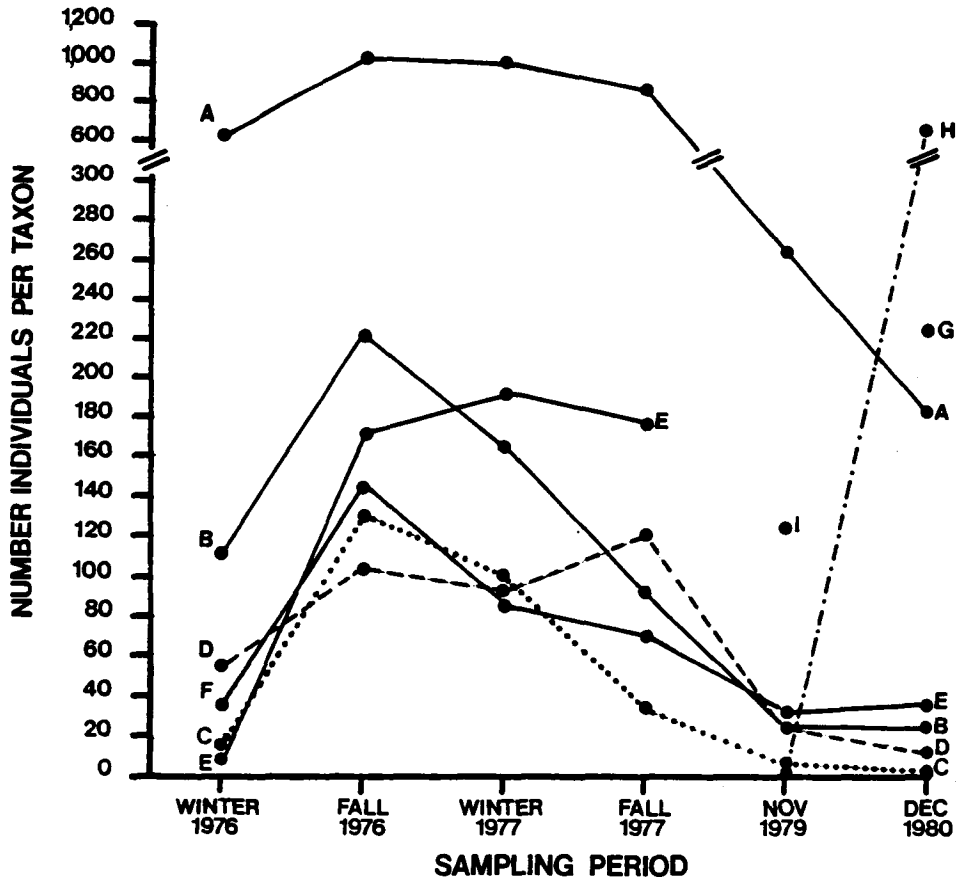


Figure 4-66. Numbers of individuals per taxon within Animal Cluster Groups A through I (from Figure 4-59), by sampling period.

and winter and fall 1977. In 1979, the number of taxa had dropped to 22, and further declined to 15 in 1980. Overall, Animal Group D was second in terms of total number of individuals (12,837); from fall 1976 through fall 1977, 10,360 individuals of Animal Group D taxa were collected. In fall 1977, Animal Group D individuals constituted 31% of the total sample; in the remaining sampling periods, Animal Group D was roughly constant in percentage abundance (range = 19% - 23%), except for 1980, when Animal Group D dropped to 6% of the total number of individuals collected. The numbers of individuals per taxon in Animal Group D show a similar pattern. In fall 1977, Animal Group D was third in number of individuals per taxon (121) at its highest value; in fall 1976 and winter 1977, the number of individuals per taxon remained roughly the same (106 and 94, respectively); lower values were recorded in winter 1976 (55), 1979 (25), and 1980 (12).

Animal Group B included eleven taxa; all eleven were present in fall 1976, winter 1977, and fall 1977, but two were absent in winter 1976 and five were missing from 1979 and 1980 samples. Overall, Animal Group B was third in terms of numbers of individuals (6,645), largely as a result of high abundances in fall 1976 and winter 1977. In winter 1976 and fall 1977, Animal Group B was reduced by about half its maximum value (fall 1976, 2442 individuals), and in 1979 and 1980 the abundance of Animal Group B was about an order of magnitude less than its maximum value had been. However, Animal Group B taxa constituted a relatively stable proportion of the total numbers of individuals present from winter 1976 through winter 1977 (13% - 15%); after this period of constancy, Animal Group B declined in percentage of individuals to 8% (fall 1977) and then to 6% (1979 and 1980). In winter and fall 1976, Animal Group B was second in number of individuals per taxon (110 and 222, respectively). Animal Group B had its highest number of individuals in fall 1976. In subsequent sampling periods, Group B suffered a steady, monotonic decline in number of individuals per taxon, dropping to fifth place by 1980 with only twelve individuals per taxon. Animal Group B was composed of two suspension feeding bivalves (Diplodonta cf. soror and Lucina amiantus); two omnivorous polychaetes Aglaophamus verrilli and Litocorsa stremma; and eight detritovores and deposit feeders, including three congeneric tube-dwelling amphipods (Ampelisca agassizi, A. cf. cristata and Ampelisca sp.), the tanaid Apseudes taylori, and the polychaetes Aricidea taylori, Prionospio cristata, and Clymenella torquata (a tubicolous maldanid polychaete).

Animal Group F included ten taxa; all ten were present from winter 1976 through fall 1977; in 1979 and 1980, seven and eight taxa (respectively) were collected from Animal Group F. Animal Group F was fourth in terms of numbers of individuals (3,852); Animal Group F taxa were most abundant in fall 1976 (1373), less common in winter 1977 (887) and fall 1977 (715), and roughly equal in abundance in winter 1976 and in 1979 and 1980 (352, 225, and 300, respectively). On a percentage basis, though, Animal Group F was most important in 1979 and 1980 (10% and 8% of the individuals collected, respectively), and ranked third overall for both years. In other sampling periods, Animal Group F ranked fourth in overall abundance, ranging from 5% - 8% of the total number of individuals collected. Animal Group F fluctuated considerably in number of individuals per taxon, ranging from a high of 137 in fall 1976, when it ranked fourth overall in number of individuals per taxon, to a low of 32 in 1979, when it ranked third overall in number of individuals per taxon. In winter 1977, Animal Group F had 89 individuals per taxon (ranked sixth overall), 72 in

fall 1977 (ranked fifth overall), and 35 and 38 per taxon in winter 1976 and 1980, respectively (ranked fourth overall in both sampling periods). Animal Group F included three taxa of omnivorous or carnivorous polychaetes: Ninoe nigripes, Sigambra tentaculata and Nephtys incisa. Animal Group F also included the gastropod Hyala sp. A. The remaining taxa in Animal Group F were deposit feeders, and included the tubicolous amphipod Ampelisca abdita; the polychaetes Magelona longicornis, Cossura delta, Notomastus cf. latericeus, and Armandia maculata; and the cumacean Eudorella monodon.

Animal Group C included only five taxa: the gastropod Vitrinella floridiana, the corophiid amphipod Photis macromanus, the cirratulid polychaete Tharyx annulosus, the spionid polychaete Prionospio steenstrupi, and the pelecypod Nuculana acuta. All were present from fall 1967 through fall 1977, while Tharyx was absent in winter 1976, 1979 and 1980 and Photis was absent in 1979 and 1980. All taxa in Animal Group C are deposit feeders, with the possible exception of Photis, which is a tubicolous suspension feeder as well as a surface detritovore (Biernbaum 1979).

Animal Group C was fifth in abundance overall (1,529 individuals). In fall 1976, when Animal Group C was at its peak, it constituted 4% of the total number of individuals of all taxa collected, thus ranking fifth among the groups. At that time, Animal Group C also had more individuals per taxon (130) than in any other sampling period. In winter 1977, the number of individuals and the number of individuals per taxon in Animal Group C dropped to 509 and 102, respectively, but Animal Group C still comprised 4% of the total number of individuals of all taxa collected. In fall 1977, the number of individuals decreased to 232, 2% of the total for all samples, and the number of individuals per taxon fell to 46. Animal Group C only made up 1% of the total number of individuals of all taxa for all samples in the other three sampling periods (73, 39, and 27 for winter 1976, 1979, and 1980, respectively). During these three periods, the numbers of individuals per taxon were the lowest recorded for any group: 18, 13, and 9, respectively. Animal Group C taxa were most common as an assemblage in Station Group 2 stations, a nearshore set of three sandy shallow sites (10-15 m deep) and one sandy deeper site (27 m) biologically most similar to one another in 1976 and 1977 (Figure 4-60).

Animal Group E included only three deposit-feeding polychaete taxa: the paraonid Paraonis sp. A, and the maldanids Asychis elongata and Asychis sp. They were collected in the first four sampling periods, but were not seen in 1979 or 1980. These taxa together included 1,650 individuals, thus ranking sixth overall. In winter 1976, they were relatively uncommon; only 31 individuals were collected, and the number per taxon was ten. In fall 1976, winter 1977, and fall 1977, Animal Group E was quite constant in numbers of individuals (512, 574, 533, respectively) and numbers of individuals per taxon (171, 191, 178, respectively), and amounted to 3%-4% of the total number of individuals of all taxa collected per sampling period. Animal Group E taxa were scattered through Station Groups 2, 3b, and 3c stations, which span the range from the shallowest, sandiest sites to the deepest, muddiest sites.

Animal Group H included only the predatory gastropod Natica pusilla. Natica was collected only in 1979, when it was quite rare (four individuals seen) and in 1980, when 686 individuals were collected, 24% of the total

number of individuals of all taxa collected. Animal Group H ranked seventh overall in abundance among the groups, but in terms of numbers of individuals per taxon was ranked first in 1980. Natica was most common at Station Group 4a stations, three sandy and silty-clayey sand stations, and at two Station Group 4b stations, one muddy and the other sandy.

Animal Group G included only the deposit-feeding synaptid holothuroid Protankyra cf. benedeni. Protankyra was collected only at a single station (I-1, having silty-clayey sand, depth 18 m) and only in 1980, when 225 individuals were seen, 8% of the total number of individuals of all taxa collected. Animal Group G ranked eighth overall in abundance among the groups, but in terms of numbers of individuals per taxon, was ranked second in 1980.

Animal Group I included only the omnivorous or carnivorous lumbrinerid polychaete Lumbrineris cruzensis. Lumbrineris cruzensis was rare in fall 1977, when nine individuals were seen. It was more abundant in 1979; 125 individuals were found, 4% of the total number of individuals of all taxa collected. Lumbrineris cruzensis was not collected in any other sampling period. Animal Group I ranked last overall in abundance among the groups, but in terms of numbers of individuals per taxon, was ranked second in 1979. It was most common at Stations IV-1, IV-4, and III-4, three sandy sites.

There were major differences between sediment texture between stations (Figure 4-67). Within stations, however, sediment texture indices based on the standard definitions of sand, silt, and clay (cf. Folk 1980) showed no statistically significant differences from one time period to the next (Friedman two-way ANOVA, $p>0.05$). Nonetheless, in very few cases did sediment texture remain constant in different sampling periods. For example, Station I-4 shifted toward muddier sediment in 1980 compared to previous years; Station II-1 became more silty in 1980 and Stations II-4, III-1, and IV-5 became more clayey in 1980.

The distributions of a number of numerically dominant taxa were correlated with one or more of the sediment texture indices (Table 4-5). The most common pattern was a statistically significant ($p\leq0.05$) positive correlation of abundance with the relative proportion of larger particles, and a significant negative correlation with the relative proportion of fine particles. Forty-one taxa (57% of 72) were positively correlated with mean grain size. Forty-nine taxa (68% of 72 dominants) were positively correlated with the ratio sand:mud; i.e. the ratio of material made up of particles $\geq$0.0625 mm in size ("sand") to that of smaller fractions ("mud"). Forty-nine taxa were positively correlated with percentage sand. Fifty-five taxa (76%) were negatively correlated with either percentage silt or percentage clay, or both. Fifty-seven taxa (79%) were negatively correlated with percentage of particles less than 0.001 mm in size. In most cases, taxa falling in this group showed both negative correlations with indices of fine particles and positive correlations with indices of coarser particles; 15 of these taxa also were negatively correlated in abundance with TOC.

Several numerically dominant taxa showed an inverse of this pattern, their abundance being positively correlated with indices of fine particles and negatively correlated with indices of coarser particles. Four taxa

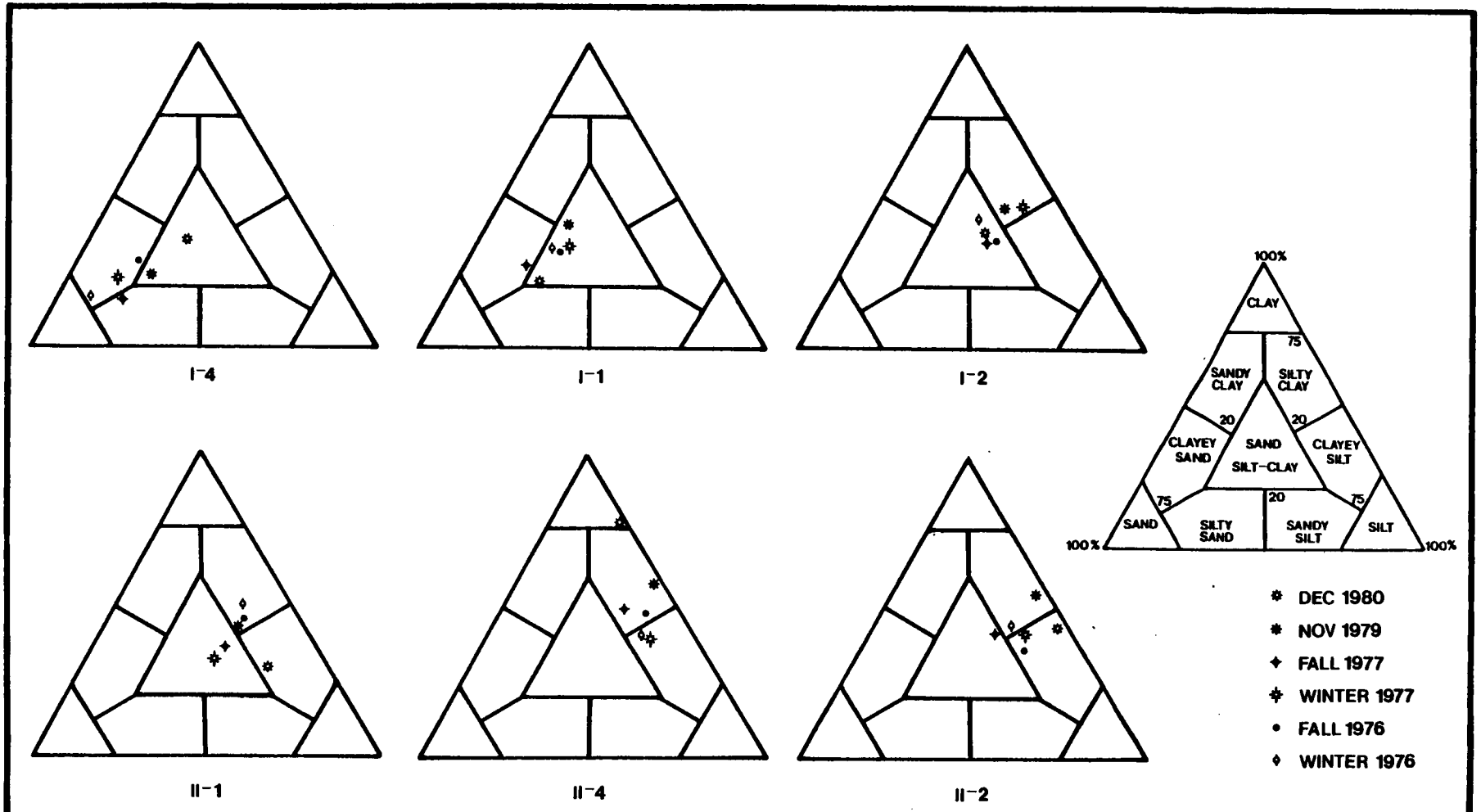


Figure 4-67. Sediment characterization by station for six sampling periods.

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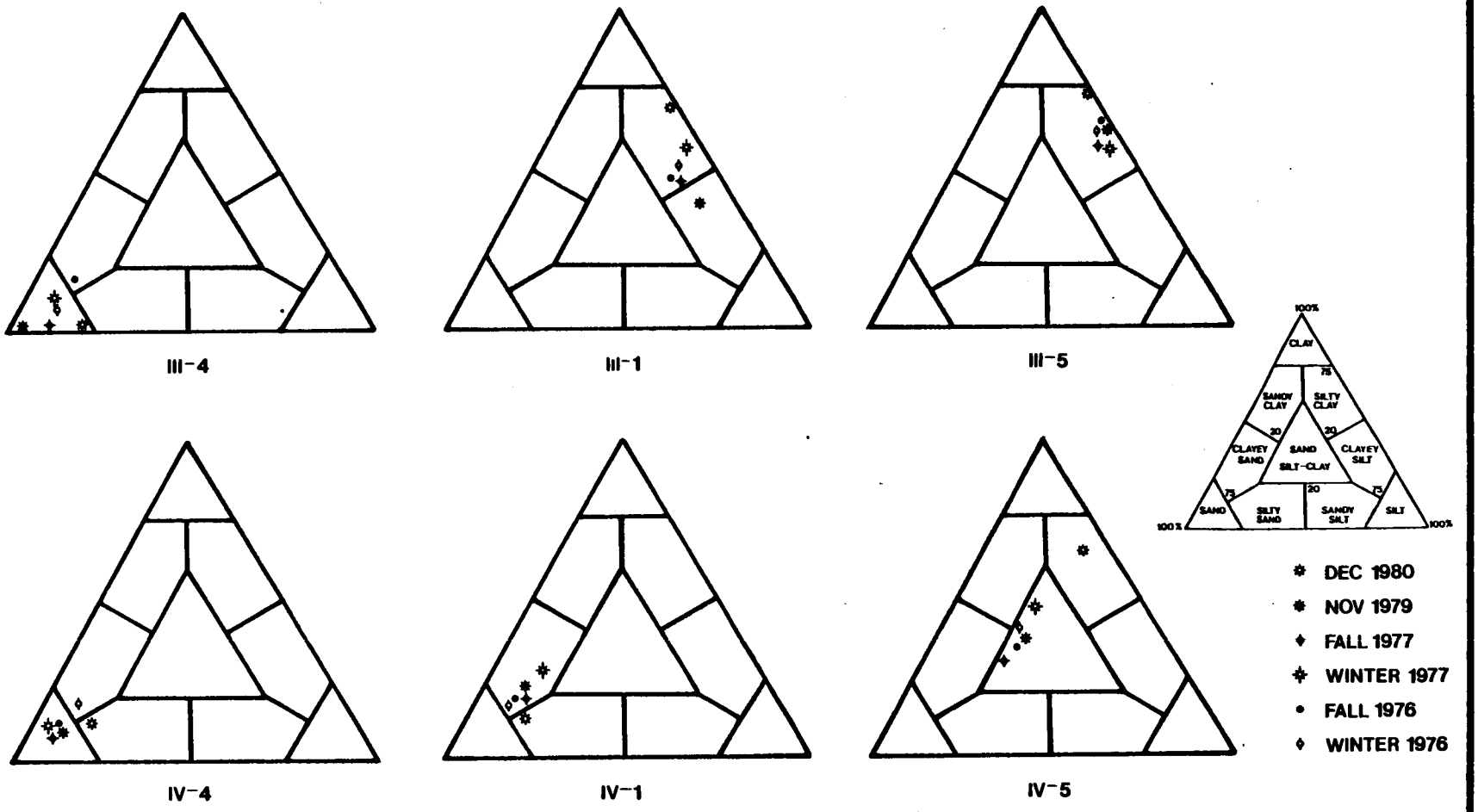

Figure 4-67 (cont'd)

Table 4-5. Results of correlation analysis of abundance of numerically dominant taxa (0.2% cutoff) with sediment parameters. S:M = ratio sand:mud (mud = silt+clay+fines); fines = particles < 0.001 mm; TOC = total organic carbon; + or − = statistically significant positive or negative correlation ($P \leq 0.05$); no symbol = no statistically significant correlation.

	CORRELATE						
Taxon	Mean Grain Size	% Sand	% Silt	% Clay	% Fines	S:M	TOC
Abra aequalis	+	+	−		−	+	−
Aedicira belgicae		+	+	+	−	+	
Aglaophamus circinata	+	+	−		−	+	
Aglaophamus verrilli	+	+	−	−	−	+	−
Ampelisca abdita				+			
Ampelisca agassizi							
Ampelisca cf. cristata	+	+	−		−	+	
Ampelisca sp.	+	+	−		−	+	
Ampelisca verrilli		+		+	−		
Anadara transversa	+	+	−		−	+	
Apoprionospio pygmaea	+	+	−	−	−	+	
Apseudes sp. A				+			
Aricidea jeffreysii	+	+	−		−	+	
Aricidea taylori	+	+	−	−	−	+	
Aricidea wassi	+	+	−		−	+	
Armandia maculata							
Asychis elongata		+	−		−	+	
Asychis sp.		+	−	+	−	+	
Caecum pulchellum			−	+	−	+	
Clymenella torquata	+	+	−		−	+	
Corbula swiftiana				+	−		
Cossura delta				+			
Diopatra cuprea	+	+	−	−	−	+	−
Diplodonta cf. soror	+	+	−		−	+	
Eudorella monodon	−	−	+	+	+	−	
Hyala sp. A	−	−		+	+		
Isolda pulchella	+	+	−		−	+	
Listriella barnardi	+	+	−		−	+	−
Litocorsa stremma	+	+	−		−	+	−
Lucina amiatus	+	+	−		−	+	−
Lumbrineris cruzensis			−		−	+	
Lumbrineris sp. nov.	+	+	−		−	+	−
Lumbrineris tenuis	+	+	−		−	+	
Magelona longicornis	−	−	+	+	+	−	
Magelona pettiboneae	+	+	−		−	+	
Magelona phyllisae	+	+	−	−	−	+	−
Magelona rosea	+	+		+	−		
Maldanidae (misc. unid.)	+	+	−		−	+	
Mediomastus californiensis	+	+	−		−	+	
Minuspio cirrifera		+			−		
Natica pusilla							

Table 4-5 (cont'd)

Taxon	Mean Grain Size	% Sand	% Silt	% Clay	% Fines	S:M	TOC
Nemertinea (misc. unid.)	+	+	-		-	+	-
Nephtys incisa	-	-	+	+	+	-	+
Nereis micromma	+	+	-		-	+	-
Ninoe nigripes	-	-	+	+	+	-	+
Notomastus cf.latericeus			+	+			
Nuculana acuta	+	+	-		-	+	
Onuphis sp.	+	+	-		-	+	
Ophiuroidea (misc. unid.)	+	+	-		-	+	
Ostracoda (misc. unid.)	+	+	-	-	-	+	
Paleanotus heteroseta	+	+	-		-	+	
Paraonidae (misc. unid.)		+	-	+	-	+	
Paraonides lyra	+	+	-		-	+	
Paraonis gracilis		+			-		
Paraonis sp. A				+			
Paraprionospio pinnata				+	-		-
Phoronida (misc. unid.)	+	+	-		-	+	
Photis macromanus				+	-		
Prionospio cristata	+	+	-	-	-	+	
Prionospio steenstrupi	+	+	-		-	+	
Protankyra cf. benedeni					+		
Sigambra tentaculata	+	+			-	+	-
Sipuncula (misc. unid.)	+	+	-	-	-	+	-
Spionidae (misc. unid.)		+		+	-		
Spiophanes bombyx	+	+	-		-	+	
Tellina versicolor	+	+	-		-	+	
Terebellides stroemii	+	+	-		-	+	
Tharyx annulosus			-	+	-	+	
Tharyx marioni	+	+	-		-	+	-
Vitrinella floridana							
Xenanthura brevitelson			-		-	+	-
Zoantharia (misc. unid.)			-		-	+	

(6%) were negatively correlated with mean grain size, with the ratio sand:mud, and with percentage sand; and also were positively correlated with percentage clay, with percentage silt, and with percentage of particles finer than 0.001 mm. These taxa were the cumacean Eudorella monodon, the magelonid polychaete Magelona longicornis, the nephtyid polychaete Nephtys incisa, and the lumbrinerid polychaete Ninoe nigripes. The gastropod Hyala sp. A also showed negative correlations with mean grain size and percentage sand, and positive correlations with percentage clay, but no statistically significant relationship with either the ratio sand:mud or percentage silt. Nephtys incisa and Ninoe nigripes were the only taxa whose abundance was positively correlated with TOC.

4.4 Discussion

The main goals originally set for LGL's portion of the impact assessment program for the Ixtoc I oil spill were to:

1. Evaluate mid-spill (November 1979) biological conditions for the macroinfaunal community at 12 stations previously sampled in the STOCS program;

2. Evaluate post-spill (December 1980) biological conditions for the macroinfaunal community at 12 stations previously sampled in November 1979 and during the STOCS program;

3. Compare and contrast pre-spill biological conditions with mid-spill and post-spill conditions for the macroinfaunal community at the same 12 stations; and, should the data from the chemical portion of the impact assessment program permit,

4. Determine whether or not observed differences in macroinfauna at the 12 stations over time (pre-, mid-, and post-spill) were correlated with the presence of Ixtoc I residues.

In fact, Goals 1 through 3 have been accomplished quite successfully, largely as a result of the use of standardized sampling methodology and coordination between STOCS personnel and LGL staff to keep taxonomic problems to a minimum. While some large taxa were not identified to the species level (e.g. the nemerteans), their appearance in nearly all samples should not be a source of too much difficulty to biologists who will recognize these groups as "catch-alls" made up of many species. LGL has had every taxonomic identification at the family level or below independently verified, in most cases by the same persons who were responsible for STOCS identifications.

For LGL to complete Goal 4 would require quantitative information on the relative amounts of Ixtoc I residues at each station. Since the sediment samples collected on site did not contain any detectable traces of oil (see Section 2), it was not possible to associate any biological changes from one sampling period to the next with the Ixtoc I or Burmah Agate spills. Therefore, this report is perhaps best considered to be an source of follow-up baseline information for 1979 and 1980 on a selected

group of 12 stations previously sampled through 1977 in the STOCS baseline program. The authors have purposely avoided use of the terms "pre-spill", "mid-spill", and "post-spill" in this report when discussing biological data, as the lack of evidence of the presence of oil in or on benthic sediments suggests that these terms might be misleading or used improperly if taken out of context. From the standpoint of the benthic organisms (based on the chemical information in this report) there was, in some senses, no spill. It is considered unlikely that hydrocarbons from Ixtoc I might have contacted benthic organisms and not left traces in the sediment (P. Boehm, pers. comm. 1982).

There is no question that major changes have occurred through time at the 12 study stations. Both numbers of taxa and numbers of individuals rose markedly between winter 1976 and fall 1976 samples, and then decreased during the next two sampling periods (winter 1977 and fall 1977). When the sites were again visited during the oil spill in November 1979, the numbers of taxa and numbers of individuals had dropped below even the winter 1976 values. One year later, in December 1980, the numbers of taxa and numbers of individuals had declined to their lowest values, about a third of the number of taxa seen during fall 1976 and about a fifth of the number of individuals.

The first sampling period (winter 1976) and the last two sampling periods (November 1979 and December 1980) shared many similarities compared to the other three sampling periods. They did not differ significantly from one another in numbers of taxa or numbers of individuals. In addition, the intervening sampling periods (fall 1976, winter 1977, and fall 1977) did not differ significantly from one another in numbers of taxa or numbers of individuals. It appears that three successive sampling periods characterized by high infaunal abundance and numbers of taxa followed one with lower abundance and numbers of taxa within a two-year time span, and were again followed by two sampling periods one year apart that resembled the first one.

The differences between the two basic groups of sampling periods (high abundance and low numbers of taxa vs. low abundance and low numbers of taxa) were not confined to a few stations; Figures 4-36 through 4-47 demonstrate that whatever factors were influencing these aspects of the biological community were acting without regard to depth or location.

Furthermore, most taxa showed the same pattern, indicating that the differences between sampling periods were not due simply to changing abundances of a few particularly common organisms. Figure 4-64 clearly shows increases in the abundance of most numerically dominant taxa in every group from winter 1976 to fall 1976, and in most cases a decline in subsequent sampling periods, with lowest values in November 1979 or 1980. The exceptions to this generalization represent highly localized increases in abundance of two taxa (one holothuroid and one gastropod) not previously collected. Both of these taxa Natica, Animal Group H, and Protankyra, Animal Group G, also proved common at other locations sampled in 1980 (see Appendices 9.3.1 and 9.3.2) indicating substantial temporal and spatial variability for these organisms. Additional corroboration for the non-specific nature of temporal differences is that the relative numerical importance (percentage of total individuals per sampling period) of each group of taxa delineated by the cluster analysis remained quite

constant over time, with the apparent drops in several groups in December 1980 being primarily a result of the sudden appearance of the two aforementioned increases (Figure 4-65). The rather similar shape of the curves in Figure 4-66 demonstrates that most taxa were best represented (greater numbers per taxon) during the three sampling periods of high overall abundance and numbers of taxa, and were present in low absolute abundances during the three other sampling periods.

The largest groups of taxa separated on phylogenetic bases also more or less retained their relative positions with respect to one another from one sampling period to the next. Polychaetes were numerically dominant in every sampling period, with deposit feeders ranked first, followed in decreasing order of abundance by errant omnivores and carnivores, suspension feeders, and those whose feeding type was undetermined. Amphipods were the largest group of crustaceans, and pelecypods outnumbered gastropods in all periods except December 1980. These groups included over 90% of the total individuals found in the study. The other groups shown in Figure 4-10 shifted ranks, largely in response to drastic increases and decreases of single taxa from one time period to the next.

A final line of evidence for the contention that changes were not only area-wide but also pan-phyletic may be found in the data for occurrences of taxa at more than one station within any given sampling period (Figures 4-50 and 4-51). In winter 1976, November 1979, and December 1980 there were consistently fewer taxa at many stations than between fall 1976 through fall 1977, when many taxa were widely distributed. In other words, under some conditions many of the taxa in the study area were ubiquitous, but during three of the sampling periods these taxa suffered restrictions in the habitats available to them.

Unfortunately, it is impossible to assign any particular cause to the pronounced differences in community structure from one sampling period to the next. It is conceptually simplest, of course, to invoke some physical factor rather than complex biological interactions, which are poorly understood for the great majority of the taxa in the area. That the differences in abundance and numbers of taxa were area-wide implies strongly that some density-independent factor(s) rather than biological interactions were involved. The gaps in time between sampling periods after the conclusion of the STOCS program were lengthy, and intervening events left no clearly interpretable record to be inferred from the data. Consequently, any attempt to attribute an observed phenomenon to its proper cause(s) has a strong tautological element.

It is tempting to speculate on possible causes for the differences seen between the three sampling periods characterized by high infaunal abundance and numbers of taxa and three other sampling periods in which infaunal abundance and numbers of taxa were low. However, it is crucial for the reader to keep in mind that life history information is incomplete for nearly every taxon included in the study, and that the static data obtained from samples collected infrequently may present a deceptively simple picture bearing little relationship to any cause-and-effect situation. For example, the numerically dominant taxa in this study were the polychaetes, which typically have pelagic larvae. The residence time of their larvae in the plankton in the Gulf of Mexico is essentially unknown. As a result, the populations of polychaetes collected in this

study may not have originated as larvae in the immediate area where they were collected. If they were present in the study area, ready to settle, and in excess of the numbers which the substrate could support, then biological conditions in the area of origin would have little or no effect upon their eventual density in the study area. If, on the other hand, the numbers of larvae in the study area were less than required to "saturate" the substrate, then densities would be directly dependent upon the abundance of larvae, which would in turn depend upon conditions between the site of origin and the study site, as well as upon the condition of the adult population which produced them. Neither the site of origin nor the conditions under which the larvae spent the earlier stages of their lives is known in this study.

Pronounced cycles in abundance are the rule, rather than the exception, for many of the taxa in this study, and it is entirely likely that the differences noted between sampling periods may be a product of natural variability rather than attributable to any single cause (human-induced or otherwise). Large fluctuations in abundance on monthly, seasonal, and annual bases are common for many infaunal taxa (Dexter 1969; Frankenberg and Leiper 1977; Moore and Lopez 1969, 1970a, 1970b, 1973; Penzias 1969; Tunnel et al. 1980; Wright and Moore 1970)

The types of physical factors which would be most likely to have significant effects on the benthic community would include major changes in bottom water characteristics (such as oxygen content, salinity, or temperature), or mechanical disturbance, especially if such disturbance altered the sediment composition (texture or organic content) to any great degree. Flint and Holland (1980) found that variability in bottom water parameters (salinity and temperature) was the most important factor in determining taxonomic abundance, diversity, and equitability. Without data from intervening periods at these sites, it is not possible to evaluate hydrographic variability with regard to the November 1979 and December 1980 collections (i.e., those of the greatest interest in this study).

Sediment texture is often the single most important determinant of macroinfaunal community components (Hargrave 1977). A detailed discussion of this subject may be found in Flint and Rabalais 1980 (Volume I, Chapter 5). Many taxa in this study can not, however, be described as sediment-limited. A large suite of taxa (mostly deposit-feeding polychaetes) dominated both nearshore, sandy sites and offshore muddy sites. These taxa included surface deposit-feeding polychaetes (Magelona phyllisae, M. longicornis, M. roseae, Tharyx marioni, and numerous spionids, especially Paraprionospio pinnata); subsurface deposit feeding polychaetes (Paraonis gracilis, Aricidea spp., Mediomastus californiensis); surface omnivorous or carnivorous polychaetes (Nephtys incisa, Lumbrineris spp.); tubicolous amphipods (Ampelisca spp.), and two phyla not identified to species level (sipunculids and nemerteans). These taxa have been described as ubiquitous in other regions as well as in south Texas (Eagle 1973, Flint and Holland 1980, Howard and Dorges 1972, Holland and Polgar 1976, Warwick and Davies 1977, Whitlach 1977).

Although both the sandy stations and the muddy stations were dominated by the ubiquitous taxa mentioned above (especially the magelonid polychaetes), some numerically abundant taxa were found exclusively at the sandy stations. These taxa included three deposit-feeding bivalves

(Tellina versicolor, Abra aequalis, and Nuculana acuta); two filter-feeding bivalves (Anadara transversa and Diplodonta cf. soror); the filter-feeding polychaete Terebellides stroemii; the predatory gastropod Natica pusilla; the deposit-feeding gastropod Caecum pulchellum; four deposit-feeding polychaetes (Magelona pettibonae, Spiophanes bombyx, Paleonotus heteroseta, and Isolda pulchella); four amphipods (Listriella barnardi, Photis macromanus, Ampelisca cristata, and Ampelisca sp. B); and the isopod Xenanthura brevitelson. That these taxa were present at three shallow stations (10 to 15 m) and one deeper station (27 m) confirms that they were not restricted by depth, but rather were confined to sandy substrates found at all four stations.

Only a few taxa appeared to be limited to deeper stations. The great preponderance of taxa found throughout the study region suggests that a more-or-less coherent community group was being sampled at all study stations, with the addition of a specialized set of shallow-water or sandy-station taxa at some locations. No clear faunal break was seen at the deeper stations, although the appearance of a few taxa not found at the sandy stations implies that perhaps the deepest stations lay near the edge of a transition zone between shallow shelf-fauna and deeper-water. The shallow-water stations therefore had greater numbers of taxa than did the deeper-water stations, in direct contrast to the results reported by Flint and Holland (1980) for three stations along one of the transects described in this study.

The study area was subjected to a major tropical storm in September 1979 (Tunnell et al. 1980), shortly before the November 1979 samples were collected. One of the most serious hurricanes ever to hit the south Texas coast (Hurricane Allen) also occurred several months prior to the collection of the 1980 samples. The evidence is mixed about the effects of heavy weather on soft-bottom benthic communities, although it can under some circumstances cause substantial changes (Rees et al. 1977), whereas under others it may have little effect (Barnett 1981).

Storms do produce water movement, reductions in salinity, and organic and sediment addition and resuspension, especially in shallow areas. The heavy rains and terrestrial erosion associated with Hurricane Allen undoubtedly caused a great deal of sediment to enter the nearshore zone of the study area. The finer fractions would remain in suspension for some time, especially nearshore where water movement is greatest, and to settle out some time later farther offshore. This transport may possibly be reflected in the data for five of the study sites (four in the 25 m to 40 m depth range, and one shallow site at 10 m depth) at which sediment texture was altered toward finer fractions (clay) in December 1980 as opposed to earlier sampling periods. The inverse of this effect (a nearshore coarsening of sediments due to removal of fine fractions) due to hurricane-generated waves was apparently observed in 1977 (Flint and Rabalais 1980, Chapter 4).

An increase in suspended sediment in the water might be expected to alter the abundance and distribution of a variety of organisms. The nearshore stations included a large number of taxa that were more or less confined to sandy habitats; a variety of these taxa are filter feeders whose feeding and respiratory apparatus may be easily clogged by the addition of fine sediments to the environment (McNulty et al. 1962a, 1962b,

O'Gower and Wacasey 1973, Paine 1961). Even the relatively mild resuspending activities of surface deposit feeders have been found to have deleterious effects on filter feeders (Levinton 1972, Rhoads and Young 1970). A shift in sedimentary regime following a major storm could have drastic effects upon these taxa. Nearshore water movement would be expected to remove fine particles rapidly by resuspension at shallower sites, however, leaving little subsequent evidence of physical change.

The deeper stations would be expected to have taxa more tolerant to fine sediments, but many of the detritus-feeding taxa at these sites are dependent upon a surficial layer of detritus settling out in areas of reduced turbulence (McNulty et al. 1962b). An increase in water motion could (temporarily, at least) deplete available food resources.

Burial of organisms and/or abrasive scour due to turbulence during tropical storms have also been shown to have significant biological effects (Jackson 1972). For example, the muddy sediment and sand communities between Sabine Pass and Point Bolivar, Texas, were essentially destroyed by the passage of Hurricane Carla (Keith and Hulings 1965).

Analyses of variance did not detect any statistically significant differences between sampling periods for sediment texture, although sediment samples were quite variable between replicates within stations. The lack of significance in the ANOVA should not be interpreted to mean that no biologically important differences in sediment texture were present, however. The ANOVA was based upon admittedly arbitrary definitions of sand, silt, clay, and so forth, using traditional size partitions to separate the categories. It would be surprising, in fact, if organisms responded to the same size criteria. One of the more puzzling features of the correlation analysis (Table 4-4) is the preponderance of taxa positively correlated with sand and coarser fractions, and negatively correlated with silt and finer fractions, yet showing few significant correlations--or positive correlations--with percentage clay. A possible cause for this apparent anomaly may be the use of arbitrary sediment size categories which may bear no relationship to those criteria which determine animal distributions. The alternative explanation is that many of these organisms do best in sandy clay but not well if percentages of silt or fines are high. The data do not permit rejection of one hypothesis in favor of the other.

Another possible cause of differences in abundance and distributions of taxa over the entire study area could have been large-scale depressions in the oxygen content of water near the bottom, resulting in hypoxic conditions in surface sediments. Hypoxic bottom water ($\leq$2 mg per litre) is a common phenomenon in the Gulf of Mexico (Bedinger et al. 1980, Harper and McKinney 1980, Ragan et al 1978). Hypoxic bottom water is typically associated with elevated concentrations of organic matter produced by erosional runoff during times of thermal stratification, producing high biological oxygen demand below pycnoclines (Gallaway 1981). Mississippi River water is the main source of hypoxic water in the northwestern Gulf of Mexico (Presley et al. 1980), which sometimes may cover the entire south Texas outer continental shelf (Flint and Rabalais 1980). While the STOCS data indicate that little density statification occurs in the study area during fall, winter, and spring (Smith 1980) and that bottom oxygen levels were generally highest in the winter (Flint and Rabalais 1980), hypoxic

benthic conditions have been documented immediately north of the study area (Gallaway and Reitsema 1981).

Whether or not hypoxic conditions could, in fact, be responsible for area-wide reductions in faunal abundance is unclear, however. Sometimes low salinities accompany low oxygen levels, and may result in widespread mortality and morbidity of polychaetes, crustaceans, molluscs, cnidarians, and other organisms (Harper and McKinney 1980). Some taxa seem to suffer when deprived of oxygen, while others seem unaffected for long periods of time. For example, nereid and sabellid polychaetes, holothurians, and hydroids have been damaged or destroyed by hypoxic, hyposaline water from tropical rains (Goodbody 1961). The abundance of spionid (Spiophanes bombyx), nephtyid, maldanid, paraonid (Aricidea and Paraonis spp.), and cirratulid (Tharyx) polychaetes has been shown to be positively correlated with benthic oxygen levels on Georges Bank, while the only taxon which increased in abundance with decreased oxygen levels was the capitellid polychaete Notomastus latericeus (Maurer and Leatham 1980, 1981). Tenore (1972) described complete die-off of all macrobenthos (capitellid polychaetes and bivalves included) at stations which became anoxic in the Pamlico River estuary.

On the other hand, burrowing infaunal organisms probably encounter hypoxic conditions rather frequently, and a number of other benthic invertebrates are capable of facultative anaerobic metabolism (Dales 1958, Eliassen 1955, Hochachka and Somero 1973).

During the warmer months, thermal stratification is typical of the nearshore waters of the outer continental shelf, with benthic temperatures commonly reaching 25° to 29° (Flint and Rabalais 1980). Dramatic reductions in temperature may occur in the study area during fall and winter. Smith (1980) reported that from late fall through early December, the thermally mixed layer extended to depths of about 75 m, beyond the outer limits of the study area, and reached low temperatures averaging 11° - 13° Celsius. However, extremely cold, dry Arctic air masses with temperatures often below freezing ("northers") frequently move through the study area, dropping water temperatures sharply. As these storms occur during a time when the water column is essentially unstratified, chilled surface water probably sinks due to increased densities, and mixes rapidly since high winds also are characteristic of northers.

The typical reproductive season for many of these taxa is during the winter (Moore and Lopez 1970a, 1970b, 1973; Penzias 1969; Wright and Moore 1970), when northers are most likely. Since most taxa increase their populations by recruitment of planktonic larvae to the benthos, and since the origin of those larvae is unknown, it is not possible to ascertain whether or not larval recruitment in the study area would be affected by any physical factor in the study area itself. For that matter, so little is known about critical temperature tolerances of nearly all of the taxa included in this study that it is not even possible to state definitively whether or not low bottom temperatures might be responsible for changes in abundances of macroinfaunal adults.

As a final caution, the authors wish to point out that in the absence of detectable residues of Ixtoc I oil in the sediments at the study sites, it is tempting to search for other catastrophic events which might have

been responsible for the pronounced declines in most macroinfaunal taxa at the 12 study sites. While we have yielded somewhat to that temptation in this section, we feel the need to re-emphasize our contention that this study is probably best viewed as a description of natural variation. The similarities between the winter 1976 data and the mid- and post-spill data are obvious. It is just as plausible to consider fall 1976, winter 1977, and fall 1977 unusually favorable seasons from the standpoint of infaunal abundance, and winter 1976, November 1977, and December 1980 more average seasons, as it is to consider winter 1976, November 1979, and December 1980 to be unfavorable seasons for macroinfaunal abundance.

Many thoughts about the effectiveness of the damage assessment strategy utilized in this study have occurred to the authors while evaluating their own data and that of the STOCS baseline program which made this project possible. While hindsight is an easy virtue, the authors would like to share some of their concerns and recommendations with readers. Virtually all biological research programs have been forced to strike a balance between the ideal and the possible with respect to resources, time, expertise, and level of resolution of data, and these comments should be viewed in the light of practical realities rather than a plea for an ultimate study design.

The decision to re-sample the STOCS stations during and following the spill using the same sampling methodology and number of replicates collected at each station was entirely reasonable. Had there been an opportunity to alter the original program, the authors would have favored the collection of a greater number of replicates at each station, even if the size of each sample had been smaller, which would have yielded a more precise estimate of population densities, but given the pre-existing STOCS data base it would have been unnecessary to take more replicates in the 1979 and 1980 collections.

One of the major problems encountered in interpreting current results was that the time of year of sample collection varied from one year to the next. As a result, the winter collections from 1976 and 1977 may not have been comparable to those taken in November 1979 and December 1980. Without samples taken during intervening periods, it is not possible to determine whether or not faunal differences might have been due to seasonal effects, for example. An even more serious problem is the gap between the end of the STOCS program and the start of sampling in 1979, and that between the 1979 and 1980 samples. Since large differences between samples taken during the same time of year from one year to the next were seen during the STOCS program, it would have been very useful to have access to data from additional samples in winter and fall of 1978, and during winter and fall of 1979, along with those from November 1979. Certainly, collecting samples at the same time of year is no assurance that hydrographic or biological conditions will be comparable in different years, but it would at least simplify the analytical tasks conceptually, and eliminate one of the multitude of uncontrolled variables that plague damage assessments in general.

Significant taxonomic difficulties occurred due to the lack of access to a complete reference collection of STOCS specimens for verification purposes. Changes in the abundances of some taxa may be artificial, resulting from identification problems which may label the same animal with

different names, for example, leading to artificial appearances and disappearances in the data set. We strongly recommend that a complete voucher collection be maintained in a central location for each such damage assessment program in the future, to avoid some of these difficulties. We were fortunate to be able to consult with many of the taxonomists involved in the STOCS program, but later groupings or splittings of taxa are quite possible, and without a reference collection it is not possible to compare new samples with older samples.

Although a recommendation for funds for additional sampling--e.g. follow-on years--is a standard ploy in ecological research programs, in this case a set of samples from 1981 would have been especially interesting biologically, since there were such marked changes in the macroinfaunal community in 1979 and 1980, compared to 1977 and 1976. Had there been petroleum residues detected in sediment, the apparent downward trend in macroinfaunal abundance could have been followed for signs of further decreases or of recovery from the spill. However, since no oil was found in sediment samples, a further measure of natural variability from one year to the next would have helped to understand the range of normal changes in the macroinfaunal shelf community, so that in the event of a spill it would be less likely that unwarranted conclusions about drastic declines might be reached.

One serious concern of the authors in evaluating the damage assessment approach used in this program is that all attention had to be focused upon the static or structural aspects of the macroinfaunal community, i.e. numbers of organisms, rather than upon the dynamics of the community. Many uncommon organisms--e.g. predators in particular--have an importance in forming and shaping a community which far outweighs their numerical abundance. This program was designed to assess large-scale changes in the most common taxa. While some might argue that any truly important modifications in community function would also, by definition, have to alter the abundances of the conspicuous forms to be recognized, the authors feel that there is not sufficient information on the biology of even the common forms to reach this conclusion. Unfortunately, we can propose no easy solution to this problem, but the gradual accumulation of life history information and toxicological response data for selected macroinfaunal taxa, for example, would go a long way toward improving the situation.

On a more practical note in the interests of economy, it would be less than honest not to mention that the authors had serious doubts about the value of analyzing the biological samples before any of the chemical results were available. As it turned out, there was no evidence of contamination of sediments with Ixtoc I oil. The most cost-effective approach the BLM could have taken in this program would have been to collect all of the necessary samples (which it did), and then simply archive the biological samples until the chemical samples had been analyzed. Upon finding oil in the chemical samples, it would have been reasonable to analyze the biological samples that were contaminated and to select a subset, perhaps, of uncontaminated biological samples for comparative purposes, rather than to analyze the entire set simultaneously. Taking this point to its logical conclusion, since there was no direct (chemical) evidence that the macroinfauna was exposed to oil, it was not necessary to analyze the biological samples at all, unless

the program goal was to collect yet another two years of baseline data (the actual, final product)!

In summary, then, future damage assessment programs would be most likely to be successful and cost-effective if they (1) utilized comparable sampling techniques and collected equivalent numbers of replicate samples; (2) were designed for high replication of each set of samples, to cope with the expected natural variability; (3) were scheduled to include samples collected at the same time of year or comparable seasons; (4) continued for at least a year or two following the suspected impact, especially if pronounced faunal changes appear to have occurred; (5) produced complete, validated reference collections of specimens; (6) worked in step-wise fashion, with chemical results preceding the further analysis of archived biological samples.

4.5 Summary and conclusions

1. South Texas Outer Continental Shelf program (STOCS) samples from winter 1976, fall 1976, winter 1977, and fall 1977 were determined to be the most directly comparable to November 1979 and December 1980 collections, from the standpoint of equivalence of replication and time of year. Consequently, comparisons were restricted to a data set from 12 stations ranging in depth from 10 m to 49 m, and which were sampled in each of these 6 sampling periods.

2. The data set described in this report included 65,166 individuals composed of 576 taxa of macroinfaunal invertebrates. There were major differences in numbers of taxa and numbers of individuals collected from one sampling period to the next, with numbers of both rising sharply from fairly low values in winter 1976 (248 taxa, 8,569 individuals) to their highest values in fall 1976 (339 taxa, 18,844 individuals). Values then gradually declined in winter 1977 (317 taxa, 15,640 individuals) and fall 1977 (318 taxa, 14,701 individuals). They subsequently dropped precipitously in November 1979 (207 taxa, 4,066 individuals) and then fell further in December 1980 to the lowest values observed (127 taxa, 3,346 individuals).

3. The November 1979 and December 1980 samples differed significantly in terms of numbers of taxa from the fall 1976 and winter 1977 samples, while periods of intermediate values (winter 1976 and fall 1977) were not statistically distinguishable from the sampling periods with either low or high numbers of taxa. The greatest similarities were seen between the three sampling periods having the largest numbers of taxa: fall 1976, winter 1977, and fall 1977.

4. The November 1979 and December 1980 samples differed significantly in terms of numbers of individuals from the

fall 1976, winter 1977 and fall 1977 samples; the winter 1976 samples had intermediate values and were not statistically distinguishable from the sampling periods with either low or high numbers of taxa. The greatest similarities were seen between the three sampling periods having the largest numbers of individuals: fall 1976, winter 1977, and fall 1977.

5. Most of the taxa considered in this study were extremely rare; 105 taxa were represented by only one individual, and 249 taxa by five or fewer individuals.

6. Diversity (H') remained relatively constant for all stations together from fall 1976 through November 1979 (range from 3.86 to 4.13), but showed the lowest values in the first and last sampling periods (winter 1976, H'= 3.55; December 1980, H'= 3.12). Evenness (V') showed a similar pattern, with low values (0.62) in winter 1976 and December 1980 and a range from 0.66 to 0.72 between fall 1976 and November 1979.

7. Most of the numerically dominant taxa spanned the depth range from the shallowest to the deepest stations in fall 1976 (40 taxa), winter 1977 (33 taxa), and fall 1977 (38 taxa), when abundance and numbers of taxa were highest. During winter 1976 and November 1979 and December 1980, substantially fewer taxa were as broad in their distributions (25, 17, and 11 taxa, respectively). The proportions of multiple occurrences of taxa rose from winter 1976 (13% at seven or more stations) to its highest value in fall 1976 (16%), and declined to 12%, 11%, and 9% in subsequent sampling periods.

8. A distinct suite of taxa was restricted to a set of three shallow (10 to 15 m) one deeper (27 m) station, all fairly near shore and having rather coarse, sandy sediment. During fall 1977, November 1979, and fall 1976 this group included 19, 17, and 15 taxa, respectively, and was reduced to twelve, eleven and ten taxa in winter 1976, winter 1977, and December 1980.

9. There were only three taxa which were rarely found at the shallowest stations. These three taxa were most common during the earlier sampling periods, and were for the most part absent from November 1979 and December 1980 samples. Other than these three, no clearly defined set of taxa was restricted to the deeper stations; the great majority of taxa common at the deepest stations were also common at the shallowest stations.

10. The abundance of most numerically dominant taxa was positively correlated with mean grain size and the proportions of coarser fractions of sediment (percentage sand, ratio sand:mud), and negatively correlated with the proportions of finer sediment (percentages of silt, clay,

and "fines" smaller than 0.001 mm). Four taxa showed the inverse of this pattern, being positively correlated with percentages of clay, silt, and "fines," and negatively correlated with percentage sand, mean grain size, and the ratio sand:mud. These four taxa also were among the eight taxa having the deepest average depth of collection.

11. The abundance of many numerically dominant taxa was negatively correlated with sediment total organic carbon (TOC). Only 2 taxa were positively correlated with TOC; these two taxa were among the eight taxa having the deepest average depth of collection.

12. Cluster analysis based upon abundance of numerically dominant taxa typically grouped stations within any given sampling period into a nearshore cluster which included the sandy stations, an offshore cluster which included the stations characterized by muddy sediments, and several lying at an intermediate distance and depth. The nearshore cluster included those stations having many broadly-distributed taxa found at all stations as well as those taxa restricted just to sandy, nearshore sites. The offshore stations included the broadly distributed taxa, and several taxa not found within the nearshore cluster. The intermediate cluster of stations usually included the broadly distributed taxa, and a reduced number of the nearshore-associated taxa not found at the deeper stations.

13. A two-way table produced by merging a cluster analysis of numerically dominant taxa and an inverse dendrogram of stations for all sampling periods suggested that at least nine distinct groups of taxa and eight distinct groups of station/periods could be differentiated. Several large-scale patterns could be seen clearly, and are described below.

14. Several groups of taxa (e.g. A and F) were important at all stations regardless of sampling period, and may be legitimately described as ubiquitous within the study area.

15. Several groups of taxa (e.g. B and C) were most important at stations having coarse, sandy sediment, and rare or absent at stations with fine sediment. The converse was not true, though. There were no groups which were primarily restricted to stations with fine sediment, but stations with fine sediment did include many of the same taxa found at sandy stations.

16. Groups of taxa (e.g. D and E) which were predominant at both muddy and sandy stations were most important during 1976 and 1977, and were less well represented at the same stations during November 1979 and 1980.

17. Unusually high abundances of several groups (e.g. G and H) at a few stations during a few sampling periods were seen; however, ubiquitous taxa (such as those in A and F) were more often responsible for "blooms," achieving relative dominance during a given sampling period or at a few stations.

18. Deposit-feeding polychaetes dominated the study area during all sampling periods (49% to 57% of the total numbers of individuals seen in any given sampling period). Another very important assemblage included errant omnivorous and carnivorous polychaetes, which were second in relative importance (16% to 20%) in all sampling periods but one. Other dominant groups (in relative order of % abundance) were amphipods (3% to 9%), gastropods (1% to 3% except in 1980 when a single taxon raised the total to 22%), pelecypods (1% to 8%), sipunculids (2% to 7%), nemerteans (1% to 7%), non-decapod crustaceans (1% to 3%), decapods (1% to 4%), echinoderms (1% or less except in 1980 when a single taxon raised the total to 7%), and other polychaetes (2% or less).

19. Since residues of Ixtoc I oil were not identified in any of the sediment samples, the temporal variations in the benthic macroinfaunal community could not be related definitely to the spill, or, for that matter, to any particular human-induced or environmental factor(s) and may fall within the range of natural variability.

SECTION FIVE

EVALUATION OF DAMAGE ASSESSMENT PROGRAM

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SECTION FIVE

EVALUATION OF DAMAGE ASSESSMENT PROGRAM

In this section the results of the IXTOC I damage assessment program are summarized, the program's methodology critiqued, and recommendations made for improving damage assessment programs in general.

5.1 IXTOC I Assessment

In spite of a massive intrusion of petroleum hydrocarbon pollutants from the Ixtoc I event into the study region of the South Texas Outer Continental Shelf during 1979-1980, no definitive damage can be associated with this or other known spillage events (e.g., Burmah Agate) on either the epibenthic commercial shrimp population (based on chemical evidence) or the benthic infaunal community. Such conclusions have no bearing on intertidal or littoral communities, which were not the subject of this study.

Drastic decreases were noted in infaunal community species abundance and diversity compared with extensive baseline information, but these changes must be ascribed to natural system variability. Detectable transport of oil to the "stable" benthic sediment system was detected north of the primary (STOCS) study region as a result of sedimentation of Burmah Agate spill residues, but was not detected anywhere within the primary study area. There is, however, strong evidence that Ixtoc oil was present in the near bottom water column system, tied up with highly mobile resuspended sediment. This material, which is difficult to sample quantitatively, has an uncertain coupling to the benthos.

Both chemical analyses and biological analyses were quite revealing. The GC/MS-based part of the chemical assessment showed that, owing to significant levels of non-petrogenic polynuclear aromatic hydrocarbons present in the sediment and chronic low level petrogenic pollution in shrimp populations, the STOCS region is not a pristine environment. The biological analyses conducted on the 1979 (mid-spill) and 1980 (post-spill) samples documented areawide changes in the benthic community compared with pre-spill (STOCS) data, decreases which most likely fell into the range of natural variability. No causal mechanisms for these changes are apparent from any of the data, but several possible environmental scenarios, including changes in bottom water characteristics (e.g. dissolved oxygen, salinity, or temperature) due to storm-induced changes or hypoxic conditions associated with elevated organic matter inputs from the Mississippi River, might serve as contributing factors. The value of a strong link between chemical and biological observation in assessing ecological damage due to a chemical spill (e.g., oil) has been unequivocally demonstrated.

5.2 Damage Assessment Methodology

The overall methodology proposed and utilized in this program (Figure 1-6) was based on two parallel lines of investigation (chemical and biological) which were designed to intersect only after each task was near completion. We have serious doubts about the value of analyzing the biological samples before any of the chemical results were available. As it turned out, there was no evidence of contamination of sediments with Ixtoc I oil. The most cost-effective approach the funding agency could have taken in this program would have been to collect all of the necessary samples and then simply archive the biological samples until the chemical samples had been analyzed. Upon finding oil in the chemical samples, it would have been reasonable to analyze the biological samples that were contaminated and to select a subset, perhaps, of uncontaminated biological samples for comparative purposes, rather than to analyze the entire set simultaneously. Since there was no direct (chemical) evidence that the macroinfauna was exposed to oil in this particular program, it was not necessary to analyze the biological samples at all, unless the program goal had been to collect two sets of updated baseline data.

With hindsight, the design decision to proceed with a copy of the baseline (STOCS) sampling program had some merit, but also some serious flaws. As Ixtoc I residues were revealed in resuspended particulate matter and not in the bulk sediment samples, we can infer that the Smith-MacIntyre sampling method, while probably sufficient for biological sampling, was inadequate in chemical samplings of the sediment. This is due to tendancy for washout of the surface layer (0-10mm) of sediment, and hence loss of any newly deposited oil. Thus the desire to both reproduce the STOCS sampling program and to use the same method for biological and chemical samplings did not address the possibility of the existence of low levels of newly deposited oil in the sediment. Pumping of bottom water in order to capture particulate oil and remote hydraulically-damped coring or diver coring to capture an undisturbed surface layer of sediment would have been better suited for chemical sampling.

The more basic question of the relationship of mobile oil residues to sight-specific biological effects remains at the center of the effort to relate chemical and biological information. In intertidal areas where oil impacts are generally higher than in offshore sediments (see for example CNEXO, 1981) a strong sediment-oil association persists for significant periods of time. Should we expect the movement of oil at low levels to an offshore environment to cause detectable changes in the biological community? At what level can changes be detected? The second question had been addressed during the study's design at which time an evaluation of the seasonal variability of the STOCS baseline data indicated that the damage assessment program was only capable of assessing large-scale (50-100% decrease) changes in the most common taxa.

One serious concern in evaluating the damage assessment approach used in this program is that all attention had to be focused on the static or structural aspects of the macroinfaunal community, i.e., numbers of organisms,

rather than on the dynamics of the community. Many uncommon organisms (e.g., predators in particular) have an importance in forming and shaping a community which far outweighs their numerical abundance. While some might argue that any truly important modifications in community function would also, by definition, have to alter the abundances of the conspicuous forms to be recognized, the authors feel that there is not sufficient information on the biology of even the common forms to reach this conclusion. Unfortunately, we can propose no easy solution to this problem, but the gradual accumulation of life history information and toxicological response data for selected macroinfaunal taxa will go a long way toward improving the situation and in answering the question "should we expect a biological change based on the low expected levels of oil in the offshore benthos?" Based on the rapid decrease in water column oil levels within 50-100km of the blowout site itself (Boehm and Feist, 1982), the answer to this toxicologically-based question is probably "no". Thus valid laboratory data acquired on water-soluble oil (Ixtoc I oil in this case) concentration levels and on the toxicological response to those levels, compared with field measurements of actual levels should have guided the decision whether to undertake a large-scale assessment program. That is, we feel that the expectation of biological change based on chemical and toxicological data should guide the damage assessment strategy.

The first phase chemical methodology used in this study was designed to fully characterize the range of possible chemical compositions of the oils which might be encountered in the environmental samples. The combined use of fused silica capillary GC, GC/MS, and stable isotope (C,H,S) analyses proved very effective in identifying floating and beached oil residues. However, GC/MS-based aromatic parameter ratios combined with isotope analyses of saturate, aromatic, and asphaltene fractions were most useful for examining highly weathered oil residues. The occasional disagreement between these methods, especially where $\delta^{34}S$ measurements indicated a near match, must be reconciled through independent research. Identifications based on organosulfur or organo-nitrogen compounds were not particularly useful in matching weathered oil residues.

The chemical strategy used to screen sediment and biological samples for possible oil residues by UV/fluorescence and followup with rigorous GC, and GC/MS analyses was quite powerful and cost effective in examining a large suite of samples for the presence of oil, and once oil had been detected, determining the exact chemical nature of the oil. Stable isotope analyses on organic extracts were not particularly useful in sourcing sediment hydrocarbons due to both the ubiquity of background hydrocarbon residues and to expected low level incremental oil increases over background levels. Only in grossly oil polluted sediment could stable isotopes conceivably play a source matching role. Stable isotope analyses on total sediment are even less well suited for oil pollution studies due to the 10-100 fold increase in background organic carbon over the organic extract.

The use of UV/fluorescence, taking into account possible quenching effects, is essential to these types of assessments. However, the detectability of low level oil residues, given biotal and sediment fluorescence

backgrounds, must be assessed by sequential oil addition experiments (Section 2) in order to make best use of resulting data.

Comparisons of chemical data acquired in this program with STOCS data were only in part useful. The comparison of n-alkane parameters, for example, revealed some very striking similarities in pre-, mid- and post-spill data, thus boding well for the use of historical data bases in general in assessment studies. Hydrocarbon to TOC ratios were also in good agreement between all data sets. With the proper intercalibration program set up, any laboratory participating successfully in such programs could be expected to achieve similar results. One shortcoming of the STOCS data base was the lack of individual aromatic hydrocarbon data with which to compare the damage assessment program data. Fortunately a limited set of such data was available from the BLM quality control program and comparison indicated good agreement between the data sets. Thus it is our conclusion that BLM data bases are quite useful for examining temporal changes.

The data bases are crucial for biological assessment programs. The decision to resample the STOCS stations during and following the spill using the same sampling method and collecting the same number of replicates at each station was entirely reasonable. Had there been an opportunity to alter the original program, we would have favored the collection of a greater number of replicates at each station, even if the size of each sample had been smaller, which would have yielded a more precise estimate of population densities. However, given the pre-existing STOCS data base it would have been unnecessary to take more replicates in the 1979 and 1980 collections.

One of the major problems encountered in interpreting current results was that the time of year of sample collection varied from one year to the next. As a result, the winter collections from 1976 and 1977 (taken in January, February, October, and November) may not have been comparable to those taken in November 1979 and December 1980. Without samples taken during intervening periods, it is not possible to determine whether or not faunal differences might have been due to seasonal effects, for example. An even more serious problem is the gap between the end of the STOCS program and the start of sampling in 1979, and that between the 1979 and 1980 samples. Since large differences between samples taken during the same time of year from one year to the next were seen during the STOCS program, it would have been very useful to have access to data from additional samples in winter and fall of 1978, and during winter and fall of 1979, along with those from November of 1979. Collecting samples at the same time of year is no assurance that hydrographic or biological conditions will be comparable in different years, but it would at least conceptually simplify the analytical tasks and eliminate one uncontrolled variable, thus strengthening the damage assessment program.

Significant taxonomic difficulties occurred due to the lack of access to a complete reference collection of STOCS specimens for verification purposes. Changes in the abundances of some taxa may be artificial, resulting from identification problems which may label the same animal with different names,

for example, leading to artificial appearances and disappearances in the data set. We strongly recommend that, to avoid these difficulties, a complete voucher collection be maintained in a central location for each such damage assessment program in the future. We were fortunate to be able to consult with many of the taxonomists involved in the STOCS program, but later groupings or splittings of taxa are quite possible, and without a reference collection it is not possible to compare new samples with older samples.

The followup analysis of a set of samples from 1981 would have been especially interesting biologically, since there were such marked changes in the macroinfaunal community in 1979 and 1980, compared to 1977 and 1976. Had there been petroleum residues detected in sediment, the apparent downward trend in macroinfaunal abundance could have been followed for signs of further decreases or of recovery from the spill. However, since no oil was found in sediment samples, a further measure of natural variability from one year to the next would have helped to understand the range of normal changes in the macroinfaunal shelf community, so that in the event of a spill it would be less likely that unwarranted conclusions about drastic declines might be reached.

Future damage assessment programs will be most successful and cost-effective if:

1. They are designed to be comparable with baseline data but modified to take into account the realities of chemical fates of oil in offshore sediments, e.g., mobile floc layers
2. They are initiated only after laboratory/field reconnaisance studies indicate likely impact based on chemical and toxicological data
3. Sufficient amounts of sample (especially in the case of chemical and isotope analyses) are available (small quantities of 1979 sediment samples precluded some isotope analyses)
4. They utilize comparable biological sampling techniques and equivalent numbers of replicate samples are collected
5. They are designed for high replication of each set of biological samples to cope with the expected natural variability
6. Sampling periods are scheduled to include samples collected at the same time of year or comparable seasons
7. They continue for some period of time following the suspected impact, especially if pronounced faunal changes appear to have occurred, so that spill-impact recovery or natural variability trends can be determined
8. A complete, validated reference collection of specimens is produced
9. The program works in step-wise fashion, with chemical results preceding the further analysis of archived biological samples
10. A multi-parameter oil identification analytical procedure is employed, and
11. A hierarchical screening/analysis chemical procedure is employed.

SECTION SIX

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ACKNOWLEDGEMENTS

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SECTION SEVEN

REFERENCES

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The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Minerals Revenue Management** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.